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THE PHASE RULE AND HETEROGENEOUS EQUILIBRIUM

by

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Preface

Classical chemistry, by which is meant not something outmoded but what is still the bulk of chemical investigation, rests upon the identification and characterization of substances and upon the study of their interaction. Implicitly or explicitly we apply the principles of the Phase Rule in almost all such considerations. Some of these principles are so clear and familiar that the systematic exposition of the theory may seem to some to be unnecessary. The subject, however, although of obvious fundamental importance, is at times only apparently simple, and deceptively so. The purpose of this book is to offer a systematic study of the meaning and application of the Phase Rule which may be general enough to be used as reference for almost any application of the principles.

Since the principles of phase diagrams are fundamentally simple, the emphasis has been placed on the interconnection between the familiar diagrams of systems of various orders, or numbers of components. The attempt has been made to point out and utilize as much as possible the basic identity of typical diagrams for a variety of relations. This includes, for example, the use of the freezing point diagrams of systems of lower order for the representation of the isothermal evaporation of systems of higher order, through the analogy between the variable of temperature for isobaric systems and the isothermal variable of water content for higher order aqueous systems.

The principal difference between the systematic exposition here attempted and that usually followed lies, perhaps, in starting with continuous miscibility in all states as the simplest possibility both in binary and in ternary systems, and introducing thereupon the complications caused by the occurrence of a miscibility gap in a particular state. A degree of generality of point of view, and of economy of discussion, seems in this way to be obtainable far beyond what can be done, in the writer's opinion, through the usual approach of introducing solid solution as a complication rather than as a fundamentally simple relation.

Although the book is concerned primarily with the underlying principles rather than with detailed examples and applications, an attempt has been made to include specific illustrations of the more important and interesting relations. The book is not intended, however, to serve as source of numerical information on any particular substance or system of substances. The accumulation of "phase rule measurements" is beyond even the capacity

of compilations such as the *International Critical Tables*. The specific examples given are therefore introduced only to make principles clearer, and they are chosen chiefly on the basis of their suitability for the purpose and their familiarity to the writer, even without regard to their importance. For some of these examples a reference to the *International Critical Tables*, a collection assumed to be generally available, has been considered sufficient, without citation of original literature.

A list of general references is given after the last chapter. Although not on so large a scale as the Roozeboom treatise, R. Vogel's *Die Heterogenen Gleichgewichte* is the most complete and general treatment of the subject. The Roozeboom treatise is a collection of expositions, by Roozeboom, Büchner, Aten, and Schreinemakers, on one-component systems and on certain aspects of binary and ternary systems. Nothing comparable to either *Roozeboom* or *Vogel* exists in the English language, and neither of these books is apparently any longer available except in libraries. The writer's debt to these and to the other general texts can hardly be indicated specifically, for among these are the things from which we have all, directly or indirectly, learned about the Phase Rule.

New York University
September, 1950

J. E. R.

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Chapter I Introduction; Meaning of the Phase Rule

Preliminary

The Phase Rule is a thermodynamic law, first stated by Josiah Willard Gibbs,¹ relating the number of phases, the number of components, and the number of degrees of freedom, or the variance, of a system in heterogeneous equilibrium, in which it is assumed that the only determinative variables are temperature, pressure, and composition. It deals with the heterogeneous equilibrium involved in processes which may be classified either as physical or as chemical, so long as they are dynamic and reversible in nature, in contrast with the nature of the static equilibrium of mechanics. The various terms involved in the Phase Rule, although familiar, require explanation and limitation for their correct application.

For preliminary purposes we shall use the following simple definitions and derivation. A phase is one of the homogeneous, mechanically separable portions of a heterogeneous system. A system consisting of a liquid and vapor is a 2-phase system, as is also the mixture of a precipitate and its saturated solution; a system consisting of a solution and two saturating solids, with vapor, is in four phases. The number of components of a system is the number of independently variable constituents necessary for the statement of the composition of all its phases, such as the number of metals, for example, in an alloy. The number of degrees of freedom (F) is the number of internal or intensive variables — various concentrations, that is, in addition to T and P — which have to be specified in order to determine the state of the system completely. The Phase Rule states that if a heterogeneous system consisting of α components in β phases is in equilibrium, then $F = \alpha - \beta + 2$. If a phase contains α components, its composition involves $\alpha - 1$ independent percentage terms, so that the total number of internal variables, including T and P , is $\beta(\alpha - 1) + 2$. But if the system is in heterogeneous equilibrium, the chemical potential of each component is the same in all phases containing it, so that there are accordingly $\alpha(\beta - 1)$ restricting conditions or equations inherent in the condition of equilibrium.

¹ J. W. Gibbs (Ref. H), *Collected Works*, Longmans, 1928, Vol. I, pp. 55–150; from *Trans. Connecticut Acad.*, 1874–78.

Hence the number of unrestricted variables, or the number of degrees of freedom, F , is $\beta(\alpha - 1) + 2 - \alpha(\beta - 1)$, or $F = \alpha - \beta + 2$.

A. Systems and Phases

In thermodynamics a system usually means a particular, isolated portion of matter subject to limited ranges of specified variables or conditions. Such a particular system, assumed to be subject only to variations in T and P , is a special case of a System in the Phase Rule sense. The Phase Rule System is a concept, which is characterized by certain chemical species or combinations of species known as its components, and which is imagined to be subject to variations of T , P , and the proportions of its components. Any particular total composition of the components is known as a complex of the System, and any such complex remains part of the System so long as the changes in T and P are so limited that the nature of the components is not changed. Since the word "system" is used in both the specific and the general sense, we shall occasionally distinguish them if necessary by capitalizing the latter, or the general, conceptual System.

The particular complex, or system, is furthermore assumed always to be a bulk sample, a quantity sufficient for the establishment of the statistical distribution of states of energy for the individual particles required for the establishment of the ordinary physical properties of the substances contained in it, and hence for the applicability of thermodynamic laws concerning large ensembles of particles. If the number of particles is too small, there can be no distinction of states of aggregation, the gas, liquid, and solid or crystalline states.

The system, at fixed T and P , is heterogeneous if it contains more than one state of aggregation, one state in more than one distinct form or kind of structure, or one state in two portions, resulting from a miscibility gap in the particular state. A system may therefore contain more than one liquid and, especially, more than one solid, so that it may be entirely liquid or entirely solid while still heterogeneous. Since a gas is statistically formless in respect to arrangement of molecules, it is expected that there may never be more than one form of this state, and that there may never be any miscibility gap in it.² Nevertheless, the liquid and gaseous states are continuous above the temperature and pressure of the critical phenomenon, and it is therefore not surprising that there should be reports of the existence of two "gas phases" at equilibrium, or of the "limited mutual solubility of gases," at sufficiently high pressure. This has been observed for systems such as nitrogen-ammonia³ and nitrogen-sulfur dioxide.⁴ Bridgman re-

² See, for example, M. Randall and B. Sosnick, *J. Am. Chem. Soc.*, **50**, 967 (1928).

³ I. R. Kritschewsky, *Acta Physico-Chim.*, U.R.S.S., **12**, 480 (1940).

⁴ D. S. Tsiklis, *J. Phys. Chem.*, U.R.S.S., **21**, 349 (1947).

marks,⁵ however, that at the high pressure involved the density of the material is so high that it would be at least as correct to speak of the observed phenomenon as the limited mutual solubility of liquids.

Any one of the various parts or forms of a heterogeneous system furthermore may be either aggregated into a single piece or layer, or more or less finely subdivided. The various fragments of any single kind of structure, separable and distinct from other forms in the same or different states of aggregation, nevertheless constitute one of the parts of the heterogeneous system. Each such part, whether continuously agglomerated or not, is considered to be homogeneous, since it is all of one form, and is known as one of the phases of the heterogeneous or polyphasic system. The various fragments of saturating crystalline salt in the system salt and saturated solution constitute a single phase; similarly an emulsion of two immiscible liquids consists of two liquid phases.

Such a phase is not necessarily constant in properties throughout, in the strict sense of the word "uniform," even if the system is at equilibrium. So long as the variations in a portion of matter are continuous, it is still considered homogeneous and hence a single phase — so long, that is, as its properties such as density, composition, refractive index, surface tension, color, interatomic distance, arrangement, etc., vary to such a small extent between adjacent points that the form of structure suffers no abrupt variations. If the non-uniformity is irregular or arbitrary, the phase is not in homogeneous equilibrium. If the system is uniform, or if its non-uniformity is regular, following, in the absence of gravitational, magnetic and other such forces, continuous patterns or statistical distributions completely and reproducibly determined by T and P , then it may be in homogeneous equilibrium. It is in homogeneous equilibrium if the prevailing distribution is independent of time and of the direction in which the equilibrium state is approached, in respect to homogeneous changes, that is, in T , P , and composition.

Variations on a very small, or micro, scale and distributed according to statistical laws of probability are possible in every homogeneous phase: variations caused by the isotopy of the elements present, random defects and random arrangements in certain crystalline phases, and the statistical variations of density, and hence of all properties, in liquid and gas phases which become so pronounced as to cause visible effects near critical points (critical opalescence). These statistical variations are reproducible functions of the variables considered in the Phase Rule and persist when the system is in final equilibrium. Phases involving only such variations may

⁵ P. W. Bridgman, *Rev. Mod. Physics*, **18**, 1 (1946).

be called not only homogeneous but uniform. Another non-uniformity possible in a homogeneous phase of an isolated equilibrium system free of the forces of gravitational and other such fields seems to be that of surface energy, if the phase is a subdivided one. The subdivided phase in a 2-phase colloidal system, for example, may not have the same surface development in all its pieces. But if there is such a thing as a reproducibly stable colloidal system, with an equilibrium state which is a function of T , P , and composition alone, independent of time and of the relative amounts of the phases, then this non-uniformity must be a regular one, following some statistical distribution fixed solely by these variables. If the colloidal system, then, is stable and in reversible equilibrium, the distribution of its surface energy must be assumed to be either uniform or a reproducible function of the stated variables. If it is not stable and not at equilibrium, it cannot be discussed in terms of the Phase Rule or represented in the terminology and by means of the graphical methods used in the Phase Rule.

Finally, it must be pointed out that, from the point of view of the Phase Rule, even homogeneity is secondary in the definition of a phase, which may also be heterogeneous. If two or more homogeneous parts of a heterogeneous system always occur in the same proportions, giving a total mass of constant composition, they constitute together a single phase, even though obviously and macroscopically heterogeneous and mechanically separable into different parts. This is the case, for example, when a solid exists in two optically enantiomorphic forms but is instantaneously and completely racemized in passing through the liquid or dissolved state. Thus solid sodium chlorate or solid quartz, in equilibrium with a melt or a solution, will consist of a 1:1 mixture of *d*- and *l*-crystals. Such mixtures may be mechanically separable into two different substances, two species with different properties, but the behavior in the heterogeneous system is that of a single phase. This is so not simply because the thermodynamic properties of the two forms are the same or even because the forms are equally probable upon crystallization, but because their ratio when in dynamic equilibrium with a melt or a solution is constant. They would still constitute a single phase if they occurred in any fixed proportion other than 1:1.

We find therefore that the term "phase" is not definable on purely physical grounds. The same is true of the expression "number of components," or the order, of a system. Just as the number of phases of a system, in the Phase Rule sense, is not a purely physical question, similarly the number of components is not a chemical question. Both terms may be said to owe not only their existence but their very meaning to the Phase Rule. They are merely aspects of that description of an equilibrium system which is known as its phase behavior. There is no general, unequivocal

definition of these terms which may be applied universally without reference to phase behavior, which means the relation between β , the number of phases, α , the number of components, and F , the number of degrees of freedom. Ultimately, it must be admitted, we have to decide, in some cases somewhat arbitrarily although always with an eye to the final relations, upon either β or α for a system, then determine F experimentally, and take the remaining term (α or β) as the unknown in the equation for the Phase Rule.

Experimentally, then, a homogeneous mass cannot be more than one phase. But a heterogeneous mass may be a single phase if, although mechanically separable, it is not separable through what we must call phase reactions, such as melting, dissolving, evaporation. Optical enantiomorphs may be separate phases of a system although identical thermodynamically. But those which, being racemized in the phase reactions of the system, cannot be resolved through phase reactions, do not constitute separate phases but a single phase of that system. This circularity of the definition of a phase seems inescapable.

Practically, however, with the special exceptions noted (distributed colloidal phases which may possibly be non-uniform, and optical or other isomers "racemized" by the phase reactions involved), a phase may be defined as one of the uniform, homogeneous, mechanically separable portions of a system in dynamic, heterogeneous equilibrium.

B. Equilibrium States

A system may be in homogeneous equilibrium in any or all of its various homogeneous portions without being in heterogeneous equilibrium between these parts, since the attainment of heterogeneous equilibrium may be slower than the establishment of homogeneous equilibrium, at least in liquid and gas phases. A system, however, cannot be in heterogeneous equilibrium without also being in homogeneous equilibrium in each of its phases. It may appear to be so only if the surface of some phase becomes so coated with an impervious layer as to isolate certain portions of matter. But then we are dealing with more than one system. True heterogeneous equilibrium, therefore, involves internal homogeneous equilibrium on the part of each phase.

It also involves dynamic, reversible interchange of matter between the phases. This transfer may occur through phases of variable composition or directly between invariable phases. The interchange between the states of aggregation of a pure substance is between phases of invariable composition, as is that in an equilibrium of three solid phases, such as $A + B \rightleftharpoons AB$, a univariant binary equilibrium, in which the proportions of the phases

depend on volume and heat content at any specified P or T . The system solid A + solid B, both pure, on the other hand, with no evidence of interchange of matter, is bivariant whether we consider it a binary system or a mechanical mixture of two unary systems. Such a mechanical mixture, with no evidence of interaction, is usually called a state of "apparent equilibrium." Those parts which show no interaction with the rest, whether present as a container, for example, or mechanically mixed, are not considered part of the system in real heterogeneous equilibrium. In such a state of "apparent equilibrium" there is no limit to the number of phases in the physical sense, no meaning in the term "phase" in the Phase Rule sense, and no point in distinguishing and counting the phases at all.

This distinction between real and apparent equilibrium, however, is not altogether easy in application. If we can establish experimentally that there is some reversible process occurring between the parts of a heterogeneous system, then the ideas of heterogeneous equilibrium may be applied. If not, we simply do not know, strictly speaking, whether or not we are dealing with negligibly small interaction or with apparent equilibrium. Thus water enclosed in a glass container and sulfur in an iron container at room temperature are cited as examples of such apparent equilibrium. Superimposed layers of liquid water and mercury, however, are considered an equilibrium system, although experimentally there may be no more evidence of interaction here than in the former cases. It may be argued, of course, that the first two systems represent states not reproducible after drastic changes of conditions, such as temperature. But this is a matter of degree, for strictly it cannot be proved that still further changes of conditions will not disclose that a particular state is not reproducible. The glass-water system, for example, is reproducible even after solidifying or evaporating the water completely. The system water-ethyl acetate, on the other hand, although an example of "true heterogeneous equilibrium," is certainly not reproducible after raising the temperature to a certain point. Such questions then are, in the final analysis, academic or extraneous to the Phase Rule; we are simply concerned with whether or not, in the range of conditions of T and P chosen for the isolation and study of the system, there is any evidence of reversible interaction. If there is, then we may speak of a state of heterogeneous equilibrium, to which the Phase Rule is applicable.

An isolated portion of matter of fixed elementary composition may exist, furthermore, at the same T and P , in a number of states of heterogeneous equilibrium, varying with respect to stability. Provided that each state is one of reversible heterogeneous equilibrium, the Phase Rule applies to all of them equally and indifferently. There is nothing in the so-called phase

behavior of the isolated system in a particular equilibrium state to give any indication about the stability of that state, provided that the range of conditions is such as to cause no variation in the nature of the components. These possible equilibrium states differ in two respects.

When the change, from the less to the more stable state, is accompanied by an irreversible change in the nature of the components, we may call the less stable state one of "false" equilibrium with respect to the more stable, or "true," equilibrium state. But it is evident that these terms may be inadequate, being at most only relative, since there may be a series of such states before a final state of maximum stability is reached. It is in this sense that van't Hoff called the materials of organic chemistry a world of false equilibrium. An equilibrium state then is known to be "false" in this sense, that is, not a state of maximum stability, if it is not reproducible upon changing the conditions of T and P without limit. Thus the System $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$ is in "false equilibrium" with respect to Systems such as $\text{N}_2\text{O-H}_2\text{O}$ and $\text{N}_2\text{-O}_2\text{-H}_2\text{O}$, etc. If the speed with which the system changes from "false" to "true" equilibrium is zero, the two states pertain to independent Systems, and the relation between them would not be suspected through the Phase Rule alone. If the transformation is instantaneous, the "false" state is unknown. With a finite rate of transformation, any number of intermediate conditions may exist and persist, and since these are not equilibrium states they will not be describable by the Phase Rule.

Strictly we may not be certain, in any given case, except perhaps in elementary Systems such as Zn-Hg , that we are dealing with "true" rather than with "false" equilibrium. At any rate, the distinction, involving a change in species and hence in the nature of the System in the Phase Rule sense, although of profound importance in chemistry, is of no interest in the Phase Rule, which applies regardless of the stability of the species in a given System. We may note, then, for later reference, that a System is defined not by its elementary composition, which is of interest only with reference to the final, most stable equilibrium state possible at specified T and P , but by the number and nature of the components involved in the phenomena studied, which is not quite the same as the notion of its chemical species — still another question. Although the application of the Phase Rule is of great value in the problem of isolating, defining, and identifying chemical substances in so far as they can act as components, it is in itself insufficient even for counting the number of chemical species in a given system, as we shall presently see.

The second difference between states of heterogeneous equilibrium for an isolated system at fixed T and P involves not a change in the identity of the System but merely a change of the phases in the same System (in the

Phase Rule sense). The less stable, now called the metastable state, is unstable with respect to some particular phase or set of phases participating in the more stable, or the "stable," state. Each state is in itself one of real, reversible equilibrium, constant in time, and approachable from either direction of change of T and P (and hence also of composition in variable phases), and therefore equally subject to the Phase Rule. The change then from a metastable to a more stable state, which itself may be metastable with respect to a still more stable state, is accompanied by a phase change and is most frequently brought about by the introduction of a nucleus of a differentiating phase. Here again we cannot be certain in any new System under investigation that any particular state is or is not a metastable one, for with regard to limited variations in T , P , and c (composition), the metastable state is not distinguishable from the "stable" state. We are not concerned, moreover, with the process or mechanism of change between such states, whether it can occur spontaneously or not, rapidly or not, etc. The Phase Rule merely recognizes that there may be states of real heterogeneous equilibrium in a single System, which are presumably unstable with respect to some particular phase also known to be possible in the System.

What is known as Ostwald's law of successive or delayed transformation may be said to apply both to the difference between "false and true" equilibrium, involving change of substances, and to that between "metastable and stable" equilibrium, involving merely change of phases, for the same substances.

C. Variance; Number of Degrees of Freedom

A particular state of heterogeneous equilibrium, for a given system of specified components, is characterized by the number and identity of the phases present. This equilibrium state is said to remain unchanged through changes of T , P , and c if there is no change in the number and nature or identity of these phases. In a system consisting of a single substance, or more generally in a one-component system, the only variables are T and P . The number of possible independent composition variables then increases as the number of components (α) increases, the number being $\alpha - 1$. The variance, F , or the number of degrees of freedom of the equilibrium state is the number of these independent variables (T , P , c) which may be arbitrarily changed without changing the defined state, or which have to be specified in order to define the particular state completely.

In testing the variance of a particular system in a particular state, that is, in the course of applying the experimental variations of T , P , and c , we find the properties of the system to vary continuously as long as the equilibrium state remains the same; and a limit is generally reached where there is a

phase transition, a change either in the number or in the identity of the phases present. This is observable as a discrete change in some measurable property of the system. Every phase in a heterogeneous equilibrium differs from its fellows in respect to either its density or its heat content, so that such phase transitions are always observable, theoretically, by dilatometry or by thermal methods; these methods will suffice at least for the present. The limitation of the physical variables to T and P may be said to imply that any phase transition must involve either a latent heat of transition or a discontinuity of density, or both.

D. The Order, or the Number of Components

This is the smallest number of composition terms (not necessarily individual, single chemical species) capable of independent variation as to proportion in the System, and necessary for the (algebraic) statement of the composition of all the phases in the equilibrium. Pure iron is a one-component system, two metals constitute a binary system, three metals a ternary one, etc. The order of such elementary systems is obvious. If, however, the substances are not elementary but compound, their possible heterogeneous interactions must be considered in order to establish the number of components.

The order of a System is then seen to be a mathematical concept. It is not an inherent physical or chemical property of the System, nor is it simply related to the number of substances or chemical species in it. It is even independent of reversible transformations of species which may occur within the range of conditions to which the System is subjected. The order is simply the number of terms of the category of composition required for the description of the Phase Rule behavior of the System. If the behavior of the System, within the specified range of T and P involved, requires no composition variable for its description, it is a one-component system, but it does not necessarily follow that it contains, even within the specified range, only one chemical species. The Phase Rule deals with the phase behavior of a system as affected by the variables T , P , c (c being the proportions of whatever is meant by its components) but not with its constitution, the question of the number and the nature of the substances in it.⁶

1. Each component itself may consist of a number of different species. An isolated sample of pure NH_4Cl contains a single component, provided that the only phases present are solid NH_4Cl and a gas, even if this gas consists entirely of separate molecules of NH_3 and HCl . A single species must behave as a one-component system, but unary behavior does not

⁶ See J. Timmermans (Ref. T), *Chemical Species*, Chemical Publishing Co., N. Y., 1940.

prove that a material is a single substance. Should the behavior of pure NH_4Cl be perfectly unary, there would be no reason on the basis of the Phase Rule alone to suspect that it is not a simple element. If, however, after complete vaporization and in the absence of proper conditions (catalyst or nucleus) for crystallization of NH_4Cl , the substances NH_3 and HCl should liquefy and solidify into phases with compositions differing from that of pure NH_4Cl , or if the restriction of stoichiometric proportions of NH_3 and HCl in each phase were removed, then the system would be binary.

In contrast, an isolated sample of pure CaCO_3 is a binary system if it involves the vapor phase besides the solid, since it dissociates into solid CaO and the gas CO_2 . Despite the fixed composition of the total system, it is necessary now to consider two components, and two are sufficient although the system contains three species. But whereas the number is fixed, the choice is free: any two of the three formulas or substances, CaCO_3 , CaO , CO_2 . With CaO and CO_2 , the phase CaCO_3 consists of $\text{CaO} + \text{CO}_2$; with CaCO_3 and CaO , the phase $\text{CO}_2 = \text{CaCO}_3 - \text{CaO}$, etc.

2. It is also possible to deal deliberately with a number of independent substances as a single component, in describing the behavior of a System. Thus in the study of the effect of T and P on the solubility of a substance X (gas or solid) in a mixed, non-volatile liquid solvent of constant composition, the System is treated as binary, so long as the only phases are pure X and a liquid solution. In certain cases the System may remain binary in behavior even if this mixed solvent is solidified; this would be the case if the solvent consisted of two thermodynamically equivalent species forming continuous solid solution of constant melting point, as for the *d*- and *l*-forms of camphoroxime.⁷ In this case, in fact, even an arbitrary change in the relative proportions of the two forms in the mixed solvent will not disturb the binary behavior, provided that X itself is optically inactive. These two forms of camphoroxime, then, are always a single component in any system involving no other asymmetry because it is never necessary to state their proportions; the proportions affect the optical rotation in this case but not the phase relations.

3. On the other hand, a pure element, even if we disregard its isotopic variety, may be binary in behavior. The element oxygen in its gaseous state may be said to contain the species O_2 and O_3 (neglecting O), each with its own distinct set of properties. If heterogeneity is brought about by cooling and compression, the system may be binary in behavior unless the proportion of O_3 has become negligible. Such a System varies only in degree, that is, in respect to the equilibrium constant of homogeneous

⁷ J. H. Adriani, *Z. phys. Chem.*, 33, 453 (1900).

transformation and in respect to speed of attaining homogeneous equilibrium, from Systems such as acetaldehyde–paraldehyde, or $\text{C}_2\text{H}_2\text{--C}_6\text{H}_6$, or *d*- and *l*-lactic acids, or even, conceivably, $\text{C}_2\text{H}_5\text{OH--(CH}_3)_2\text{O}$. If in each case the substances mentioned were the only possible species for the given total elementary composition, then, with infinite or at least sufficient time to reach homogeneous interspecies equilibrium in every phase, they are all unary. With no interspecies equilibrium, they are all binary. With observable speed of transformation, they are classified as unary, but pseudobinary, Systems.

The number of components, then, of a System, or its order, is not an inherent property but part of the description of its Phase Rule behavior under the specified range of conditions of the isolation and study of the System, a mathematical concept derived from the observation of its phase behavior under specified conditions: the smallest number of symbols or formulas (representing either actual individual substances or arbitrary but constant combinations of such), capable of independent variation in their proportions, required to represent algebraically the composition of all the phases of the system. "Composition," of course, is much more than elementary composition, for there would otherwise be no distinction between O_2 and O_3 or between the *d*- and *l*-forms of tartaric acid. Composition means the proportions of whatever is meant by the components, which may differ solely in respect to some physical property. The number of species or of substances in a system may therefore be greater than the number of components in it, both because the components may form new additional species by combination, displacement, and metathesis, and because a component itself is not necessarily a single substance.

Like the question of the number of phases, the idea of the number of components is completely definable only with reference to the application of the Phase Rule to the particular equilibrium state under consideration. It is part of that description. Unless this circular dependence upon the Phase Rule itself is realized, the definition according to Gibbs, of the number of components as the number of independently variable constituents, may be criticized as being vague and ambiguous. It has accordingly been suggested that the term α of the familiar equation $F = \alpha - \beta + 2$ be replaced by the quantity $\alpha' - r$, α' being the total number of constituents, or the "actual chemical substances," of the system, and r the number of distinct (presumably independent) chemical reactions that can take place in the system.^{8, 9} But again there is no unequivocal method for counting the

⁸ P. van Rysselberghe, *J. Phys. Chem.*, **36**, 1733 (1932), citing the suggestion of T. de Donder, *Leçons de Thermodynamique et de Chimie Physique*, Paris, 1920.

⁹ S. T. Bowden, *Nature*, **141**, 331 (1938).

number of "constituents" in a real system, and furthermore for determining how many *independent* chemical reactions take place in the system, except by application of the Phase Rule. If carbon and oxygen are brought to equilibrium at some fixed values of T and P , the system may consist of two phases, pure carbon and a gas containing CO , CO_2 , and O_2 . The four "constituents," C , CO , CO_2 , O_2 , take part in at least four reactions: $\text{C} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}$, $\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2$, $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$, $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2$. The number of these reactions to be considered independent, at the specified T and P , depends on the observed variance of the system. If it is bivariant, then it is known from the Phase Rule that α , or $\alpha' - r$, = 2, so that only two of the reactions are independent. But as the temperature is lowered, the system may become trivariant or even quadrivariant, whereupon α must be taken as 3 (or 4) and r as 1 (or 0). The problem of determining the number of independent constituents is replaced by that of finding the number of independent reactions, in itself no less vague and ambiguous. In some cases the consideration of the difference $\alpha' - r$ instead of simply α seems indeed to be an unnecessary exercise, for we may imagine a great number of "constituents" in $\text{H}_2\text{O} + \text{CuSO}_4 + (\text{NH}_4)_2\text{SO}_4$, and always find the right number of chemical reactions to leave the number of components three, if we know that the only phases of the system are additive in respect to these three or any other three formulas. It is not the notion of "constituents" and their interaction but the required number of analytical formulas or recipes that is the significant meaning of α in the Phase Rule.

We shall now point out some simple rules for the determination of the order of Systems.

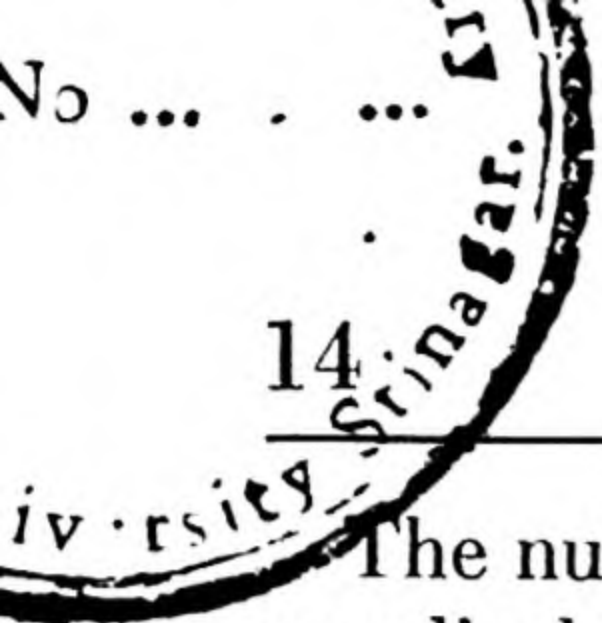
If the System does not involve reactions of the nature of displacements or double decompositions, and the more complex phases are merely additive in respect to simpler phases, then the System is binary if all the phases can be produced, additively, from two phases, ternary if all the phases can be so produced from three phases, etc. Thus the 3-phase system CaCO_3 (solid), CaO (solid), CO_2 (gas) is binary, as is also the system $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$ forming a solution and various hydrates. The system $\text{Na}_2\text{O--SO}_3\text{--H}_2\text{O}$ is ternary since all the known phases are additive in respect to these three substances. All alloy systems, in which all the phases are either the separate metals or their additive combinations, are of this class, namely, *additive systems*.

Otherwise, the substances involved either in a simple displacement reaction or in a double displacement (double decomposition) constitute three components. The displacement system, iron–water–iron oxides (hydrated or anhydrous)–hydrogen, has the three elements Fe , H , O as its components, and may still be considered as an additive system. The metathetical system consisting of four solids BaCO_3 , Na_2SO_4 , BaSO_4 , Na_2CO_3 , known as a

reciprocal system, with or without a melt of these substances, is also ternary. Any phase may be represented in terms of any three of the four salts, negative quantities being permitted in the algebraic expression of the composition; thus $\text{pure BaCO}_3 = \text{BaSO}_4 + \text{Na}_2\text{CO}_3 - \text{Na}_2\text{SO}_4$.

Although there are four interchanging radicals (or ions) in this system, these ions are not independently variable in their proportions, and they may not be used in any way as the components of the system. Although there may be a choice in regard to the nature of the components in a system, and although even the number of components is not simply a question of the chemical constitution of the system, we do find that the notion of component is related to the constitution to this extent, that only entities capable of independent existence and hence of independent variation in their proportions in a complex may serve as components. Only true chemical substances or species, or definite combinations of such, can be components of a system. Although we may not infer the number and nature of the substances in a system from its components in the Phase Rule sense, we may say, on the other hand, that a chemical species or a substance must be something which *can* act as a component in such a sense. The ions are fundamentally concepts by which we explain the interaction in the above system, but they are not substances with independent, characteristic, individual properties or capable of separate existence and independent variations in proportions, as is the case with an entity such as Na_2SO_4 itself.

The system salt-water is binary only in the absence of hydrolysis. Hydrolysis here means a heterogeneous interaction or double decomposition between the salt and water, resulting in a phase the composition of which cannot be expressed additively in terms of the salt and water as the only components. Whatever happens to the acidity of the solution is of no concern to us unless it affects the system in the manner indicated, through phase reactions. Thus the system $\text{FeCl}_3\text{-H}_2\text{O}$ is binary as long as the only solid phases are ice, FeCl_3 , or hydrates of FeCl_3 and as long as the vapor, if present, is pure H_2O or $\text{H}_2\text{O} + \text{FeCl}_3$. The system $\text{BiCl}_3\text{-H}_2\text{O}$ is ternary because oxy-chlorides appear as solid phases, and the system $\text{NaHCO}_3\text{-H}_2\text{O}$ is also ternary when the vapor consists of $\text{H}_2\text{O} + \text{CO}_2$. If in these cases the salt itself may be considered as a compound of two oxides, one metallic the other non-metallic, it is often convenient to take as the components these oxides and water, so that the system $\text{NaHCO}_3\text{-H}_2\text{O}$ becomes a part of the ternary system $\text{Na}_2\text{O-CO}_2\text{-H}_2\text{O}$ and the system $\text{Bi(NO}_3)_3\text{-H}_2\text{O}$ a part of the system $\text{Bi}_2\text{O}_3\text{-N}_2\text{O}_5\text{-H}_2\text{O}$. In the case of a chloride this procedure is not possible, and the components of the system $\text{BiCl}_3\text{-H}_2\text{O}$ are taken as any three of the four substances BiCl_3 , H_2O , BiOCl , HCl , negative quantities being used in expressing the composition of one of the phases.



The number of components then in a system of three salts all possessing a radical in common, and therefore incapable of metathesis, such as three sulfates, is, of course, three. With water added, the system becomes quaternary, provided that there is no hydrolysis on the part of any of the salts. If there is hydrolysis for any or all of them, the system becomes quinary, since the maximum number of components will be five: water, three metallic oxides, and SO_3 . A system of water and a reciprocal salt pair is quaternary in absence of hydrolysis, and similarly becomes quinary if any hydrolysis has to be considered.

If isotopy is considered, an ordinary "pure" substance containing an element with two isotopes is, strictly speaking, a binary system. Even if the proportion of the two isotopes is constant in the system as a whole, the case is not different from the over-all fixed stoichiometric proportions in pure CaCO_3 , which is binary. The isotopic mixture will not show, strictly, unary behavior but a melting point varying with the relative amount of phase change, and a vapor pressure at constant T varying with the proportion vaporized, etc. Ordinarily such differences are beyond experimental detection, but systems such as H_2O – D_2O and HBr – DBr , for example, are studied as binary systems in the usual way. For ordinary purposes, however, natural isotopic mixtures known as "pure substances" are to be treated as single substances.

E. Deduction of the Phase Rule

The quantities of the α components of the system are the masses $m_1, m_2 \cdots m_\alpha$. The unit of quantity may also be taken as the arbitrary "mole," such as "60 g of acetic acid." The units m and n (number of moles) are then related by a factor which is constant from phase to phase, so that the following considerations are unaffected. But the substitution of n for m is in this case of no fundamental chemical significance, being only a convenience for the purpose of chemical arithmetic or stoichiometry. The true molecular transformation would require a factor possibly differing from phase to phase and itself a function of T , P , and c . At any rate, the thermodynamic derivation of the Phase Rule does not refer to the constitution of matter, whether or not it consists of molecules, and whether or not it is composed of various elements.

If we distinguish the components by means of subscripts and the phases by superscripts, the Gibbs free energy (called the zeta potential, ζ , by Gibbs) of the polyphasic system is

$$G = G^1 + G^2 + \cdots + G^\beta. \quad (1)$$

In each phase the variation of the free energy with respect to T , P , and the quantity variables is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, m_1, \dots, m_\alpha} dT + \left(\frac{\partial G}{\partial P}\right)_{T, m_1, \dots, m_\alpha} dP + \left(\frac{\partial G}{\partial m_1}\right)_{T, P, m_2, \dots, m_\alpha} dm_1 \\ + \left(\frac{\partial G}{\partial m_2}\right)_{T, P, m_1, m_3, \dots, m_\alpha} dm_2 + \dots + \left(\frac{\partial G}{\partial m_\alpha}\right)_{T, P, m_1, \dots, m_{(\alpha-1)}} dm_\alpha, \quad (2)$$

or

$$dG = -\eta dT + V dP + \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_\alpha dm_\alpha, \quad (3)$$

in which η is the entropy and V the volume, and in which μ_1^1 is defined (by Gibbs) as

$$\mu_1^1 = \left(\frac{\partial G^1}{\partial m_1^1}\right)_{T, P, m_2^1, \dots, m_\alpha^1} \quad (4)$$

With dn_1^1 instead of dm_1^1 , this derivative would be called the partial molal free energy of the component 1 in phase 1, but in either case it may be called the chemical potential of the component in that phase.

For a reversible, equilibrium change at constant T and P , in each phase, then,

$$(\partial G)_{T, P} = \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_\alpha dm_\alpha = \sum_\alpha (\mu_\alpha dm_\alpha) = 0, \quad (5)$$

which is the condition for homogeneous equilibrium at constant T and P . But also, for the heterogeneous equilibrium of the polyphasic system,

$$dG = dG^1 + dG^2 + \dots + dG^\beta = 0, \quad (6)$$

so that at constant T and P ,

$$\sum_\beta \left[\sum_\alpha (\mu_\alpha^\beta dm_\alpha^\beta) \right] = 0. \quad (7)$$

The number of variables to be determined at constant T and P in order to define the system completely is $\alpha\beta$, the quantities of α components in β phases. These are to be determined by the restricting conditions of the system. The internal conditions are obtained by consideration of equation 7, the general condition for heterogeneous equilibrium at constant T and P . Expanded, this means

$$\left[\begin{array}{l} \mu_1^1 dm_1^1 + \mu_2^1 dm_2^1 + \dots + \mu_\alpha^1 dm_\alpha^1 \\ + \mu_1^2 dm_1^2 + \mu_2^2 dm_2^2 + \dots + \mu_\alpha^2 dm_\alpha^2 \\ \vdots \\ + \mu_1^\beta dm_1^\beta + \mu_2^\beta dm_2^\beta + \dots + \mu_\alpha^\beta dm_\alpha^\beta \end{array} \right] = 0. \quad (8)$$

This equation must be satisfied, at constant T and P , for a reversible change or transfer of components between the phases. If there were no connection between the quantity variations (dm 's), the equation could generally hold

only if all the potentials (μ 's) were zero. But since the system is isolated and the total quantity of each component in the system is constant, then

$$dm_1 = \sum_{\beta} dm_1^{\beta} = 0. \quad (9)$$

This furnishes α (one for each component) external restricting conditions, based on the fact that the isolated system is a particular complex with a fixed quantity of each component.

In addition to these α external restrictions, there are two classes of internal restrictions connected with equation 8 — the internal conditions of interphase equilibrium, and the composition restrictions furnished by the possible presence of phases of restricted, though not necessarily invariable, composition. These composition restrictions are of the form

$$dm_{\alpha}^{\beta} = 0, \quad (10)$$

signifying that the component α is not a constituent of the phase β . Every such restriction removes one term from equation 8. For the remaining terms we find it necessary and sufficient to assume that the chemical potential, μ , of each component is equal in every phase in which that component is present, or that

$$\begin{aligned} \mu_1^1 &= \mu_1^2 = \cdots = \mu_1^{\beta} = \mu_1; \\ \mu_2^1 &= \mu_2^2 = \cdots = \mu_2^{\beta} = \mu_2; \\ &\vdots \\ \mu_{\alpha}^1 &= \mu_{\alpha}^2 = \cdots = \mu_{\alpha}^{\beta} = \mu_{\alpha}. \end{aligned} \quad (11)$$

Then the polynomial of equation 8, reduced by the number of terms equal to the number of composition restrictions, may be factored vertically to give

$$\mu_1 \sum_{\beta} dm_1^{\beta} + \mu_2 \sum_{\beta} dm_2^{\beta} + \cdots + \mu_{\alpha} \sum_{\beta} dm_{\alpha}^{\beta} = 0, \quad (12)$$

which must hold because of equation 9. The sum of the restrictions, given by equations (10) and (11), or the sum of the composition restrictions and the interphase restrictions, is easily seen to be $\alpha(\beta - 1)$, which may be called the number of internal restrictions of the particular equilibrium system. Together with the α external restrictions from equation 9, this gives a total of $\alpha\beta$ restrictions, equal to the number of variables to be determined. Hence the equality of the chemical potential of each component in every phase containing it is seen to be the necessary and sufficient internal condition for heterogeneous equilibrium.

At this point, in order to derive the Phase Rule, a shift is introduced in the nature of the $\alpha\beta$ variables which are to be determined, the masses of

the α components in the β phases — changing them for the purpose from $\alpha\beta$ equivalent quantity variables, each being a term with the unit m (or n , if we had so chosen at the start) to a mixture of variables with two sorts of units, the masses of the phases and their percentage compositions (or the total number of moles of each phase, and their mole percentage compositions). Unless this substitution is clearly realized the result will be a certain degree of confusion and ambiguity in the application of the Phase Rule itself. The total number of variables remains the same, or $\alpha\beta$, since there are β masses of phases, and $\beta(\alpha - 1)$ independent composition variables, the percentage of one of the components in each phase always being calculable as a difference. The β phase-masses are now classified as external composition variables since the equilibrium state is independent of these masses, and the $\beta(\alpha - 1)$ percentage terms are classified as internal composition variables. But neither of these two kinds of variables — masses of phases, and percentages in phases — is equivalent to the thermodynamic quantity variable of equations 2 and 7, the quantity of an individual component in an individual phase, in a system of specified quantity of each component. Neither the mass of a phase nor its percentage composition can be introduced in any way into the thermodynamic equations 2, 7, in place of the variations dm_α^β . Unfortunately, these “ dm ” or “ dn ” variations are frequently called variations in concentrations or in composition, but they are actually quantity variations, in unit and in meaning; they are thus used by Gibbs, always. If, for example, the quantity of a phase consisting entirely of the component α is increased by the quantity dm_α in the course of a reversible change in an isolated system in heterogeneous equilibrium, the change is clearly a real one thermodynamically but appears to be nothing from the point of view of “concentration” or “composition” of that particular phase. We see then why, with the use of the notion of composition as the intensive variable in place of the true quantity variable required thermodynamically, a variation in composition can be applied as a determinative variable only with reference to variable phases. Otherwise this limitation in the application of the composition variable to variable phases comes later as a disturbing discovery in the application of the Phase Rule, since no distinction between the quantity variables is made in equations 2 and 7.

Leaving this subject for the moment and returning to the derivation of the Phase Rule, we note that there are then $\beta(\alpha - 1)$ internal variables, the independent composition variables in each phase, in addition to the two intensive variables T and P , to be determined by the $\alpha(\beta - 1)$ internal restricting conditions, the equalities of the chemical potentials and the composition restrictions, of the system. Hence the variance F , the number of

intensive and internal variables not automatically fixed by the internal conditions, or the number of degrees of freedom, is given by the equation

$$F = [\beta(\alpha - 1) + 2] - [\alpha(\beta - 1)] = \alpha - \beta + 2, \quad (13)$$

which is the Phase Rule.

Examples of variance:

Invariant systems or states: $F = 0$ when $\beta = \alpha + 2$. Such states are therefore referred to as triple, quadruple, quintuple points, etc., in unary, binary, ternary systems, etc., respectively.¹⁰

Univariant equilibrium: $F = 1$ when $\beta = \alpha + 1$; this is sometimes called "perfect heterogenous equilibrium" since all the variables are determined by the arbitrary specification of a single condition. The 2-phase equilibrium of liquid and vapor for pure water and the equilibrium saturated salt solution + vapor for a binary system of salt and water are examples.

Bivariant states: $F = 2$ when $\beta = \alpha$. Examples are water vapor (or any pure substance in a single phase), unsaturated salt solution + vapor, etc.

Trivariant states: $F = 3$ when $\beta = \alpha - 1$. A variance greater than two is possible only in systems containing more than one component, so that a composition variable is introduced in addition to those of T and P . The following cases illustrate states with increasing F . The statement, "a saturated aqueous solution of a solid, + vapor, at specified T ," is a complete definition of a system (binary) since $F = 2 - 3 + 2 = 1$. The same is true of the statement, "a saturated aqueous solution of two solids, forming separate solid phases, + vapor, at specified T ," for three components, since again $F = 3 - 4 + 2 = 1$. But "a saturated aqueous solution of two solids forming continuous solid solution, + vapor," is not completely defined by specifying the temperature alone, since the composition of the solution depends on the composition of the solid; $F = 3 - 3 + 2 = 2$. If the same system is subjected to a pressure higher than that required to condense all the vapor, leaving only two condensed phases, then $F = 3$, and even specifying both T and P now does not define the system.

F. On the Application of the "Composition Variable" as a Degree of Freedom

Consider the univariant equilibrium of the binary system A-B in the following three phases: a liquid solution containing both components, a vapor (pure B), and pure solid A. One arbitrary variation of an intensive or internal variable is possible without changing the equilibrium state. If

¹⁰ According to Gibbs (Ref. H), I-97, "It is entirely improbable that there are four co-existent phases of any simple substance."

the vapor is pure B and the solid pure A, the variation may be T , P , or the composition of the liquid solution; but no variation is possible in the pure phases if "composition" is understood to mean "percentage composition." There is nothing in the usual derivation of the Phase Rule to restrict the "composition variable" as a determinative degree of freedom to one phase and not to another, nothing to say that we cannot completely define the system by arbitrarily stating the T , the P , or the "composition" of *any* phase. Yet it is clear that specifying either that the solid is pure A or that the vapor is pure B does not define the system, whereas T , P , or the composition of the variable phase, the liquid, does define it.

Because of this apparent difficulty, it has seemed necessary to some to assume that all phases are variable, or that there is never any pure phase in a heterogeneous equilibrium. Accordingly all solids are considered solid solutions, and this school of thought meticulously indicates (or apologizes for not indicating), in all diagrams of binary and higher systems, all solid phases as variable solid solutions always containing all the components of the system, presumably in order not to "contradict" the conclusions of the Phase Rule.¹¹ This may be called the "Phase Rule argument" for the "universality of solid solution." Two other arguments are sometimes advanced. The atomistic argument states that since matter in any form always contains empty space besides atoms and molecules, the space in it is always to some extent available for holding some atoms or molecules of a foreign substance. The argument seems unanswerable for the gas phase, and still reasonable for any liquid, but certainly not convincing for close-packed solid phases characterized by definite arrangement. Even atomistically it does not seem necessary or likely that crystals of NaCl in equilibrium with an aqueous solution of some very large and complex organic molecule must contain that component in solid solution. At any rate the Phase Rule is a thermodynamic law and would hold even if matter were continuous. Another argument states that zero concentration of a component in a phase is impossible since its chemical potential would then be minus infinity, according to the equation $\mu_1 = \mu_0 + RT \ln a_1$, in which μ_0 is the chemical potential in the pure component as standard state and a_1 the "activity" of the component in the actual phase. But this equation does not necessarily imply that $\mu_1 = -\infty$ when $c_1 = 0$. With the pure component as standard state we introduce the concentration together with an activity coefficient, and set the coefficient equal to 1 when $c_1 = 1$, but we cannot say what the value of the coefficient will be when $c_1 = 0$, when it may be either infinite or indeterminate. Certainly it is not found necessary

¹¹ A. C. D. Rivett (Ref. O), *The Phase Rule*, Oxford University Press, London, 1923; J. S. Marsh (Ref. K), *Principles of Phase Diagrams*, McGraw-Hill, N. Y., 1935.

to assume that every component is present in every phase in order to derive the Phase Rule.

As for the "Phase Rule argument," the answer is found in the inadequacy of the "percentage composition" as a substitute for the rather complicated quantity variable used in the deduction of the Phase Rule. The true volume concentration, grams or moles per unit volume, of a component in any phase containing it, whether the phase is pure or variable, would solve many but not all cases of this kind of difficulty.¹² Thus, in the example already cited, if we specify the density of A in the pure solid A, or the density of B in the pure gas B, we find the system to be completely defined. But while this appears satisfactory, the density of a phase in a heterogeneous equilibrium cannot be arbitrarily controlled or fixed; it is not an experimental or operating variable, even when it is determinative. But now let us consider, besides, a compound AB, formed in the same system, with congruent melting point. At specified T and P , it is possible for the pure solid compound to be in equilibrium with two different liquid phases, the composition of the liquid phase depending on whether the total system consists of AB + excess of A or AB + excess of B. Even the density of AB (together with statement of either T or P) is now insufficient to define the bivariant system without reference to the total composition. In fact, we find now that, unless this total composition is known, even the temperature and pressure fail to operate as determinative degrees of freedom. Hence the general solution to the "problem" is not the assumption of universal solid solution or the variability of all phases; but neither is it the use of volume concentration as the composition variable.

If the total composition is known, however, and if the quantity variable is used in the terms in which it is used in the derivation of the Phase Rule, then and only then may the two degrees of freedom of such binary systems (solid AB + liquid solution) be chosen freely from the three equivalent variables T , P , and a quantity variable in any phase whatever. This correct quantity variable is the mass of one of the components, such as A, in any phase, pure or variable, in a system containing known, definite masses of the two components A and B. But such a variable is cumbersome, not easily plotted as just a third coordinate together with T and P , for example, for the graphical representation of the binary system, whereas percentage composition (c) does fulfill this practical requirement. No difficulties are encountered, of course, in plotting T , P , and c as the coordinates, but it must be remembered that this c is not the true quantity variable required for the meaning and application of a determinative degree of freedom in its complete and general sense.

¹² J. E. Ricci, *J. Am. Chem. Soc.*, **57**, 805 (1935).

Whether, then, a particular solid phase in a particular equilibrium system is to be considered as pure or not, or as invariable or variable, is a matter of experiment. Theoretically it is not necessary that the phase be variable. "Pure" means pure within the limits of observation, and if a phase appears to be pure we gain simplicity of representation and discussion, without contradicting any theoretical requirement, by assuming that it is pure. Indeed, we may note that if there were theoretical grounds for expecting all phases to be impure, there would be no reason for distinguishing systems of different orders, that is, of different numbers of components. All systems would contain all components, and the very idea of the Phase Rule would disappear.

Despite the indeterminateness of "composition" as a degree of freedom when applied through phases of invariable composition, it is nevertheless entirely possible and correct to represent all the possible equilibrium states of systems in terms of the coordinates T , P , and one composition coordinate for every component over one.

G. Graphical Representation of Phase Equilibria

Since the only variables in a one-component system are T and P , a plane figure with these coordinates is sufficient for the "phase diagram" of such

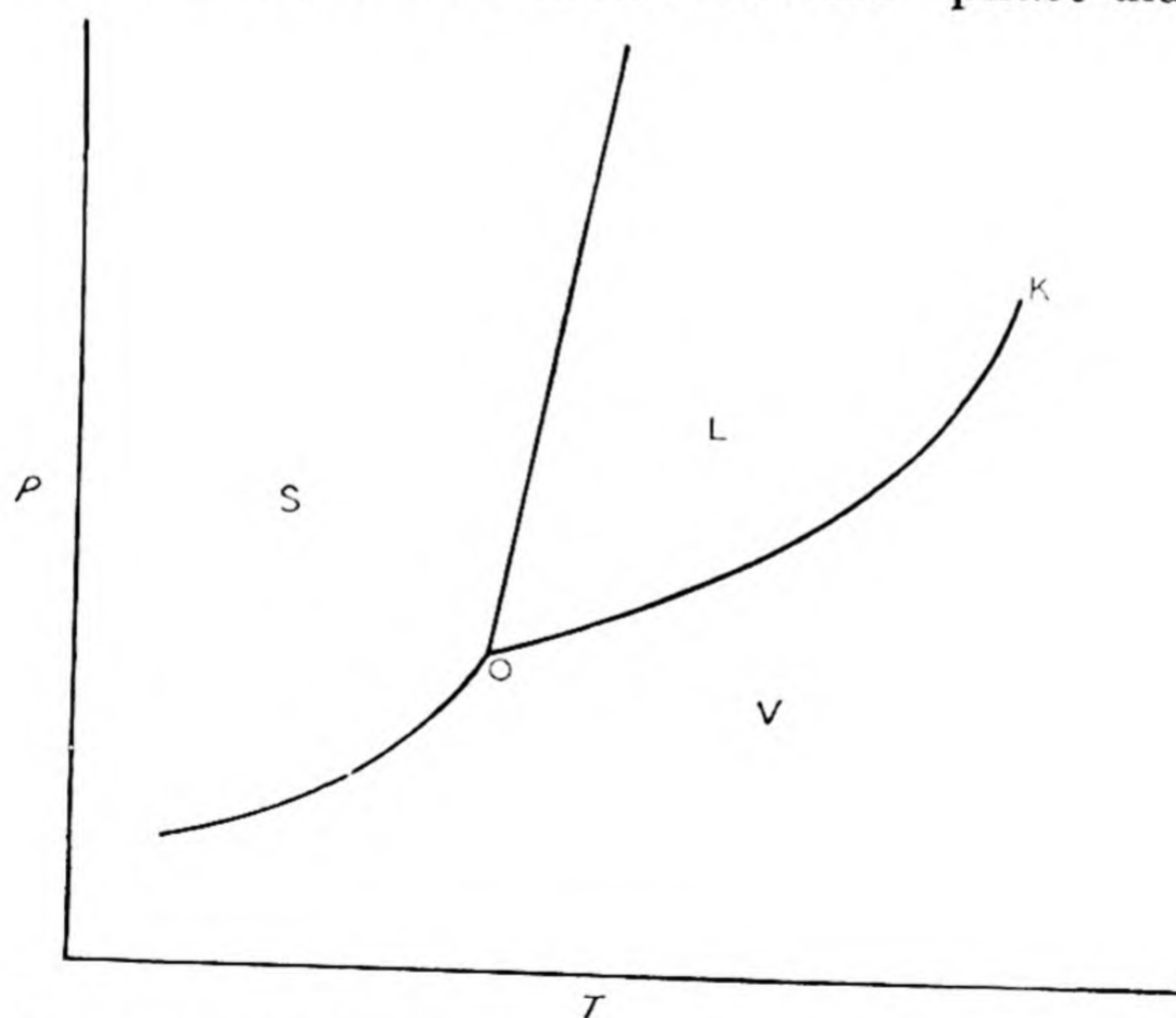


FIG. 1-1. Phase diagram of one-component system.

a system. Every phase (S , solid, L , liquid, V , gas) of the system, constituting a bivariant equilibrium state, is defined by an area, with two degrees of freedom. Univariant, 2-phase equilibria are defined by lines or curves, and invariant equilibria, or triple points, such as point O of Fig. 1-1, are

the points of intersection of three such curves. Such a diagram, known as the P/T diagram, is then said to *define* the system, by indicating the number and kind of phases coexisting at equilibrium for various values of T and P . But the diagram tells nothing about the difference in properties between the two phases coexisting along any curve, except that, proceeding to the right (isobarically, with increasing T) through any curve, the transition is from a phase of lower to one of higher heat content, and proceeding vertically (isothermally, with increasing P) through a curve, the transition is to a phase of greater density. Nor does the diagram give the relative proportions of coexisting phases, except at point K.

At point K of Fig. 1-1 the liquid L becomes identical with the phase V, the conditions are singular, literally critical, and this is a critical point. Not only are its coordinates critical values of T and P , but since the two phases at this point become identical, there is a particular and critical value of any property of the system as a whole when these phases become identical at the critical point, so that there is a critical density, critical entropy, critical refractive index, etc. But in addition and for this very reason, the actual quantities of the two phases also become identical at the point K, so that this is the only point at which the diagram specifies anything about the relative quantities of coexisting phases. The proportions at all other points on the curves depend on the density and heat content of the sample. The fields for L and V are seen to be continuous around the point K. This means that there is no significance in the distinction between L and V except along the univariant curves of the diagram, which are known as phase boundaries of the diagram. This presentation of the $L = V$ critical point is classical, we may say, and highly simplified from the point of view of modern statistical considerations concerning a region of heterogeneity which may be said to persist above the critical point in the van der Waals sense, or above the temperature at which separation into two layers, L and V, ceases to be possible. This phenomenon, involving molecular clusters not large enough for the development of surface tension for interphase separation, offers a possible explanation of the fact that the "critical phenomenon," that is, the disappearance of a meniscus, is observable over a range of specific volume of the substance, a circumstance otherwise usually attributed to impurity.¹³ But such discussion concerns a detail in the pressure-volume relations in the neighborhood of K and does not modify the main relations

¹³ J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Wiley, N. Y., 1940; especially p. 312; also, J. E. Mayer and S. F. Harrison, *J. Chem. Phys.*, 6, 87 (1938). The situation, however, is not clear. According to O. K. Rice, *Chem. Rev.*, 44, 69 (1949), the P/V curve is expected on thermodynamic grounds to have a finite horizontal section at the critical point, but to be nevertheless always sloping above it.

here presented; it is important from the point of view of molecular theory, not of the Phase Rule. Wherever the gross distinction visible as a meniscus between L and V disappears, that point will be called the critical point.

The use of a plane P/T diagram for the representation of the phase relations of a one-component system assumes that the equilibrium relations depend only upon T and P . Whenever the behavior of a one-component system is represented on such a plane, with P and T as coordinates, it is assumed and understood, implicitly or otherwise, that all other effects (surface, magnetic field, gravity, etc.) are absent, ignored, constant (even if unknown), or completely determined by P and T . Otherwise each additional variable requires the introduction of another dimension in the graphical representation, together with modification of the Phase Rule itself.

A binary system is completely defined, in representation, by a three-dimensional figure with the coordinates P , T , c , where c is the composition in weight percentage or mole fraction. This is called the space model of the binary system. It consists of two kinds of spaces separated by various surfaces. Some of these spaces are imagined to be filled with what may be called phase points representing the composition of a variable binary phase. Each such space is a trivariant equilibrium, giving the coordinates (P, T, c) for a single, continuous phase. In the case of a phase of invariable composition, the space reduces to a plane, an isoplethal plane, or one of constant composition. In the other class of spaces are those between the phase spaces or phase planes, which comprise consequently the bivariant, 2-phase equilibria. The coexisting phases in such an equilibrium, always of course at the same T and P , lie at the extremities of tie-lines (conodes, joins), isothermal, isobaric straight lines which are imagined to fill the bivariant space and to generate its bounding surfaces, which are then the limiting compositions of the coexisting phases: curved surfaces for phases of variable composition and planes for pure components or definite compounds. Tie-lines (always isothermal and isobaric) common to two such bivariant spaces and therefore connecting the compositions of three coexisting phases, may be said to generate ("ruled") surfaces of univariant equilibrium. Finally, a tie-line common to four such univariant, 3-phase surfaces, and therefore joining four coexisting phases, is an invariant state involving four phases of fixed composition at fixed P and T .

An isobaric section of this space model is therefore a plane, with T and c as coordinates, known as the $(T/c)_P$ diagram. Now the individual phases are defined by areas, if variable in composition, or by straight lines (isoplethal), if constant in composition. These are the isobarically bivariant fields of the diagram. Two-phase, isobarically univariant equilibria are also areas, but they are filled with isothermal tie-lines joining the bounding

phase fields or phase lines; and a tie-line common to three such areas marks an isobarically invariant, 3-phase equilibrium.

Again such diagrams may be used for the representation of the phase relations of a binary system only if it is known or at least assumed that the only determinative variables in the equilibrium are P , T , and c . If the variable of specific surface or surface energy, for example, is not assumed to be reproducible for any given value of T and c on the isobaric diagram, then the plane T/c plot is not to be used (without qualification). Such a plot, to be interpreted, must be assumed to imply that, unless the surface effect is negligible, it is either constant or inherently and reproducibly determined by T and c alone. Otherwise we cannot infer that the points presumably generating a curve on the T/c diagram do belong even to the same curve. The surface energy, or at least the statistical distribution of the surface energy of any phase, must, like its specific volume, be assumed to be a function of P , T , and c alone. When this requirement is satisfied, even colloidal systems (e.g., soap-water) are subject to the Phase Rule and are representable by means of the usual graphical methods in which the variables are P , T , and c .¹⁴ But when this requirement is suspected of not being fulfilled, such diagrams by themselves, involving the unknown and unreproducible variable of surface, cannot be interpreted as phase diagrams.

H. Effect of Additional Restrictions

1. A system may be studied at some arbitrary, constant value of a particular condition, such as constant P or constant T . Such externally applied restrictions are of great practical importance, but their significance is merely that of a partial derivative as compared to a general derivative. At constant P or T the (operating) Phase Rule becomes $F = \alpha - \beta + 1$, and at both constant P and constant T , $F = \alpha - \beta$. The equilibria in higher order systems, such as quinary aqueous salt systems, are sometimes studied under the condition of saturation with respect to a particular salt such as NaCl; this condition is equivalent to reducing both α and β by one, and the operating Phase Rule remains unchanged.

2. More interesting are the restrictions, which we shall call "equality restrictions," arising from the nature of the system itself and connected with certain particular relations between the phases in equilibrium. These equality restrictions are of two classes, namely, critical and non-critical phenomena. A critical phenomenon is one which occurs when two coexisting phases, in the same or different states of aggregation, approach and attain identity in all properties, thereby merging into a single phase. Even

¹⁴ J. W. McBain, R. D. Vold and M. J. Vold, *J. Am. Chem. Soc.*, **60**, 1866 (1938).

the quantities of the two phases involved are equal when the critical phenomenon occurs. A non-critical phenomenon, in this sense of an equality restriction, occurs when two coexisting distinct phases, at least one of which is variable, are the same merely in composition. In this case the relative proportion of the two phases is not fixed but depends on the volume and the heat content of the system. This involves the relation which will later be discussed as the congruence of the composition of two different phases, in contrast to the critical identity of two conjugate portions of the same phase; it is in the latter category that we place the critical phenomenon of L and V in the theory of "corresponding states."

Either type of equality restriction, demanding particular values of the variables, such as the compositions of coexisting phases, may be said to reduce the freedom of the system in the equilibrium state in which they occur. For this reason it has sometimes been proposed⁹ to "extend" or "generalize" the Phase Rule, in order to include such restrictions ($= R$), into the expression

$$F = \alpha - \beta + 2 - R. \quad (14)$$

The implication, however, that a particular value of the variance, such as $F = 0$, has the same physical or thermodynamic meaning, whether or not it is the result of an equality restriction, requires examination.

Let us consider the case of invariance, or $F = 0$, according to equation 13. If a system is invariant because $\beta = \alpha + 2$, it maintains its equilibrium state, and hence its intensive variables, unchanged against changes of volume or of heat content by means of phase transformations, until one of its phases is consumed. Hence such systems, like water at its triple point, or $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at its transition point, the quadruple point $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{aq. Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{vapor}$, can be used as thermostatic controls and as thermometric references. This property of such systems, however, which is an immediate and important implication of the word "invariance," requires that the equilibrium state be independent of the relative amounts of the phases in it. This is not so in systems in which $F = 0$ because of a critical phenomenon acting as a restriction, so that any attempt to change the volume or the heat content of such a system results in a change in the equilibrium state and hence in the intensive variables. For example, CO_2 at its critical point has a singular value for its specific volume and specific heat content. A binary system at its upper or lower consolute or critical solution point, in which the phases are two identical liquids in equal amounts and a vapor, has not only singular values of T , P , and compositions of the phases, but also, for every total composition of the polyphasic system, a definite over-all specific volume and over-all

specific heat content. Such systems are obviously not invariant in a real sense. Similarly, whereas the incongruent melting point of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, an equilibrium involving four phases in a binary system, is a source of constant temperature, the congruent melting point of a hydrate such as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is not. The binary, 3-phase equilibrium, solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + liquid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + vapor (practically pure H_2O), is a singular point, with $F = 0$ "by restriction" (since the solid and the liquid phases have the same composition), but it is not invariant in any real sense. The addition of heat to the system, for example, causing vapor to form at the expense of the other phases, changes the composition of the liquid, with resulting change in the temperature. If the system is condensed, to eliminate the vapor phase, then the melting point is a function of the pressure. If the three phases of such a system — vapor, liquid, and binary compound — all have the same composition, then the system is really invariant, but it is no longer binary but unary — thus, presumably, for NaCl in the "system" sodium-chlorine, which, practically, means two different systems, sodium-sodium chloride and sodium chloride-chlorine.

A system will therefore be called invariant only if $F = 0$ because $\beta = \alpha + 2$. If $F = 0$ because of any kind of equality or identity restriction, on the other hand, it will be called a "singular point," since it is distinguished by singular, particular, or critical values of the variables T , P , c , but it is incapable of maintaining the constancy of these conditions through phase transformations.

Furthermore, the liquid-vapor equilibrium of a binary system is bivariant, and with the restriction that the liquid and gas phases shall have the same composition (azeotropic binary solutions) the equilibrium becomes univariant-by-restriction, since, for example, the values of P and c are fixed by a single variable, T . But the system is not univariant in the same sense that the liquid-vapor equilibrium of a one-component system is univariant, in which the isolated system may be subjected to an arbitrary variation in T without changing the defined equilibrium state, here merely the number and nature of the phases. In the azeotropic case an arbitrary change in T upon the isolated system either causes one of the two phases to disappear or causes them to become different in composition; in either case the defined equilibrium state is destroyed. The only meaning of $F = 1$ for this system is that all such individual systems or complexes of the general System fall on a continuous curve, with a unique relation between T , P , and c , in the space model of the System, and it is clear that the term "univariant," even by restriction, is likely to be misleading as a statement of the relations, unless the distinctions here brought out, between equation 13 and equation 14, are kept in mind.

The number of equality restrictions (R of equation 14), moreover, is not always simply the number of pairs of phases of the same composition. This is so only for critical phenomena, so that $R = 1$ for the identity $L = V$ or for the identity $L_1 = L_2$, in a system of any number of components. The concept, however, otherwise requires careful application. For example, the polymorphic forms of calcium carbonate in the system $\text{CaO}-\text{CO}_2$ do not constitute such a "pair." Similarly, although the three phases of pure water at its triple point have the same composition, no such "restriction" is involved. As for the identity of composition of a solid and a liquid phase, the value of R depends on the order of the system. If a binary compound C melts, in a binary system, to a liquid of composition C , then $R = 1$, so that the 2-phase equilibrium of solid C and liquid, with $C = L$ in composition, is univariant, while the equilibrium of solid C , liquid, and vapor, with $C = L$, is invariant by restriction. If a ternary compound D , however, melts in a ternary system to a liquid of composition D , then $R = 2$, for it is necessary to fix two independent composition variables to specify a ternary composition; hence the equilibrium of solid D , liquid and vapor with $D = L$ in composition, is invariant by restriction.

3. Finally, in addition to "equality restrictions," we shall consider also the effect of composition restrictions of the nature of equation (10). These restricting conditions are imposed by the presence of pure phases in the equilibrium or by the condition that certain of the components occur in only a restricted number of phases of a particular equilibrium state. Under such circumstances certain of the components of the system may be excluded from participation in the actual phase reaction of the equilibrium state, and those phases containing the non-participating components are not essential to the equilibrium state. The phase reaction then involves only a restricted number of components, and may be called a phase reaction of *lower order*, or perhaps a degenerate equilibrium state. The variance of such a system is determined only by the components and phases participating in this lower order phase reaction. If, for example, an equilibrium state involves two solid polymorphic forms, A_1 and A_2 , of a pure component A , and other condensed phases of any number of substances, it is univariant, since the phase reaction is that of one component in two phases. Whatever the composition and number of the other phases, then, the equilibrium state is either isobarically or isothermally invariant. At a specified pressure the temperature of the equilibrium must be that of the unary system at the same pressure. Similarly, let us consider an aqueous salt system in which one of the salts, A , forms a dihydrate and a monohydrate, existing as pure solid phases. If the equilibrium state involves — together with other phases, liquid or solid — the three phases $A \cdot 2\text{H}_2\text{O}$, $A \cdot \text{H}_2\text{O}$, and vapor

(pure H_2O), then it is univariant, since the phase reaction, $\text{A} \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{A} \cdot \text{H}_2\text{O} + \text{vapor}$, is that of a binary system in three phases. The system is isothermally invariant whatever the number and nature of the other phases present, and its vapor pressure is that of the simple binary equilibrium at the specified temperature. This isothermally invariant state, therefore, falls on a *point* of the isothermal phase diagram of a ternary system under its own vapor pressure, or what will later be called the *condensed* isothermal diagram; it falls on an *isopiestic curve* of the condensed isothermal diagram of a formally quaternary system, and on an *isopiestic surface* of the corresponding diagram of a formally quinary system.

Since invariance seems incompatible with a curve or a surface, the effective order of the system in such a lower order equilibrium state is better calculated from the variance and the actual number of phases present. If the phases of the isothermally invariant system are $\text{L} + \text{A} \cdot 2\text{H}_2\text{O} + \text{A} \cdot \text{H}_2\text{O} + \text{V}$ (pure H_2O), then the effective order $= F + \beta - 2 = 3$, since $F = 1$ and $\beta = 4$. Such a system is effectively ternary, then, whatever the number, nature, and proportions of the substances present in the liquid phase; at the same time the phase reaction itself is of still lower order, being binary. Whereas, in other words, an aqueous system containing four salt components is expected to require four solid phases in addition to the liquid and vapor for isothermal invariance, the solution saturated with the hydrate $\text{A} \cdot 2\text{H}_2\text{O}$ becomes invariant during isothermal evaporation when it begins to precipitate the lower hydrate $\text{A} \cdot \text{H}_2\text{O}$ as second solid phase. This invariance can be explained only by considering the system as ternary rather than quinary.

We may distinguish then the formal or *synthetic order* of the system, determined by the number of substances used in its preparation, and the *effective order* determined experimentally from a particular equilibrium state. When there is no known synthetic order, the relation between the effective order and the "true order" may remain always a question. If we extend the range of variation of the conditions of T and P in the attempt to have the effective order represent the "true order," we must keep in mind that the range must be so limited as not to cause a change in the nature and number of the components, so that the search presupposes the answer. With a completely unrestricted range of conditions we ultimately count not components but the elements and their isotopes. The Phase Rule is of necessity, or by definition, restricted in its application to a range of conditions such as not to change the nature and number of the components of the system. Hence one of the terms of the Phase Rule equation, ultimately the order α , cannot be determined independently of the observed terms, F and β .

Still another characteristic of a system undergoing a lower order phase reaction remains to be mentioned. During the equilibrium phase reaction the non-participating phases are not only invariant in composition but also constant in actual amount, since they contain substances not involved in the reaction. In the isothermal evaporation of the aqueous salt system consisting of the condensed phases $L + A \cdot 2H_2O + A \cdot H_2O$ the liquid remains constant not only in composition but also in actual amount until all of the dihydrate has been decomposed, at equilibrium, to the monohydrate. Similarly if a system consisting of ice and a solution of salts is evaporated isothermally, the phase reaction involves only the component water in unary sublimation. The system is therefore isothermally invariant and the solution, containing substances not involved in the phase reaction, is not only invariant in composition but "inevaporable" or constant in actual amount. This would be true even if the multicomponent solution were saturated with some salt hydrate in addition to ice. If pure ice and pure water vapor are involved, the equilibrium is still isothermally invariant regardless of the complexity of the solution and of the nature and number of other phases present. Various examples of such "inevaporable solutions" were pointed out by Meyerhoffer,¹⁵ but his explanation, which was not general or clear, has subsequently been somewhat confused.¹⁶

These relations will be illustrated and elaborated further in connection later with the study of systems of more than one component. They are mentioned here to illustrate the point that the "order" of a system is merely part of the Phase Rule description of the particular behavior under observation. Some of the equilibrium states of a system of α independent substances can only be understood, in other words, on the basis of a system of order less than α , even aside from equality and identity restrictions.

¹⁵ W. Meyerhoffer, *Berichte*, **30**, 1810 (1897).

¹⁶ A. Findlay, *The Phase Rule and Its Applications* (Ref. G), Longmans, London, eighth edition, 1938; p. 196.

Chapter II One-Component Systems

A. Phase Diagram and Property Diagrams

As an example of a system in which the only phases are S, L, V, we shall consider water at pressures below $\sim 2000 \text{ kg/cm}^2$, the ordinary form of ice (ice I) being known to change to ice III at 2115 kg/cm^2 and -22°C . Fig. 2-1 shows the three fields in which the system consists of a single phase, the lines along which it consists of a mixture of phases of two adjacent fields, and the point O at which all three phases coexist at equilibrium.

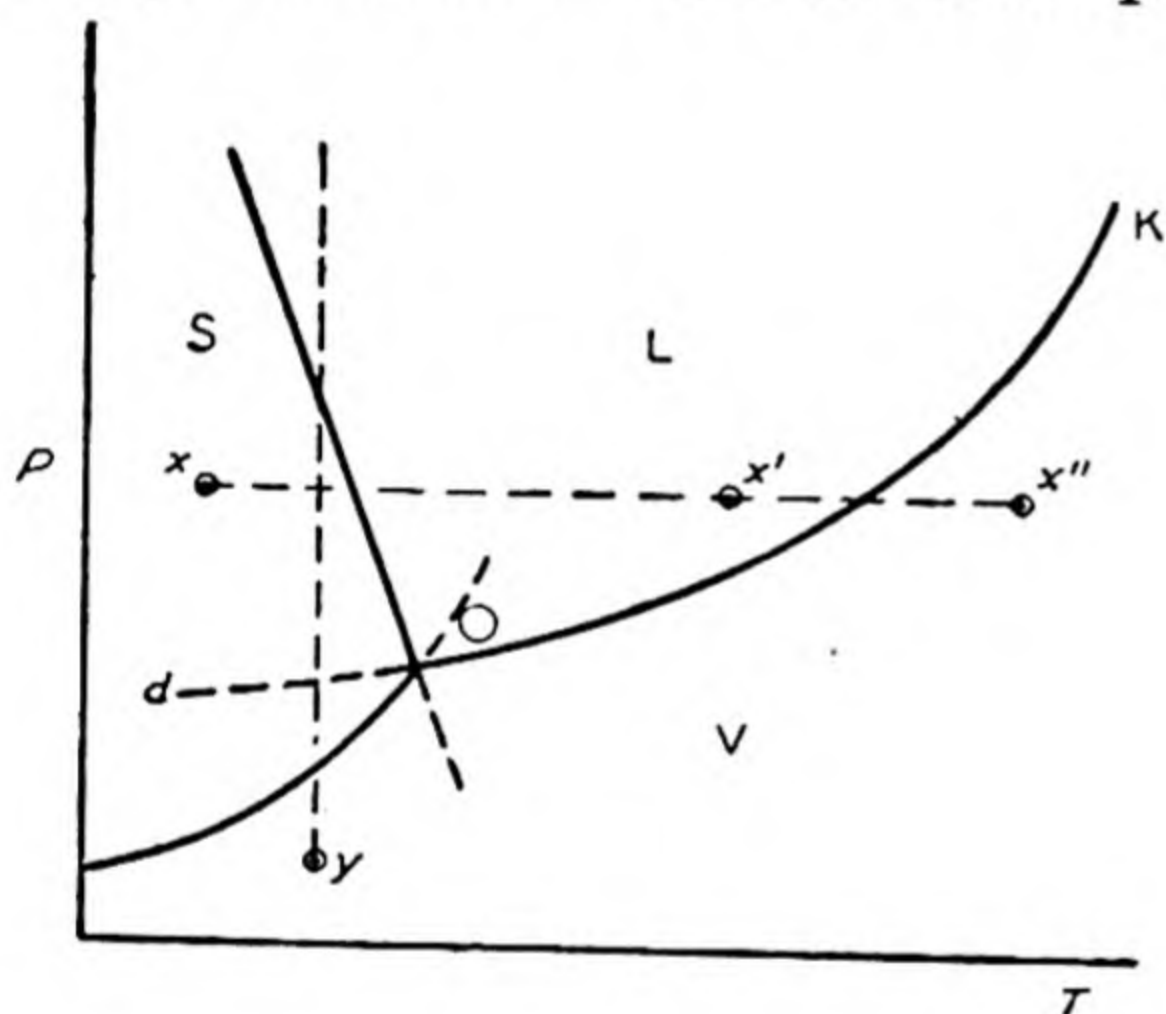


FIG. 2-1. P/T diagram for water (schematic).

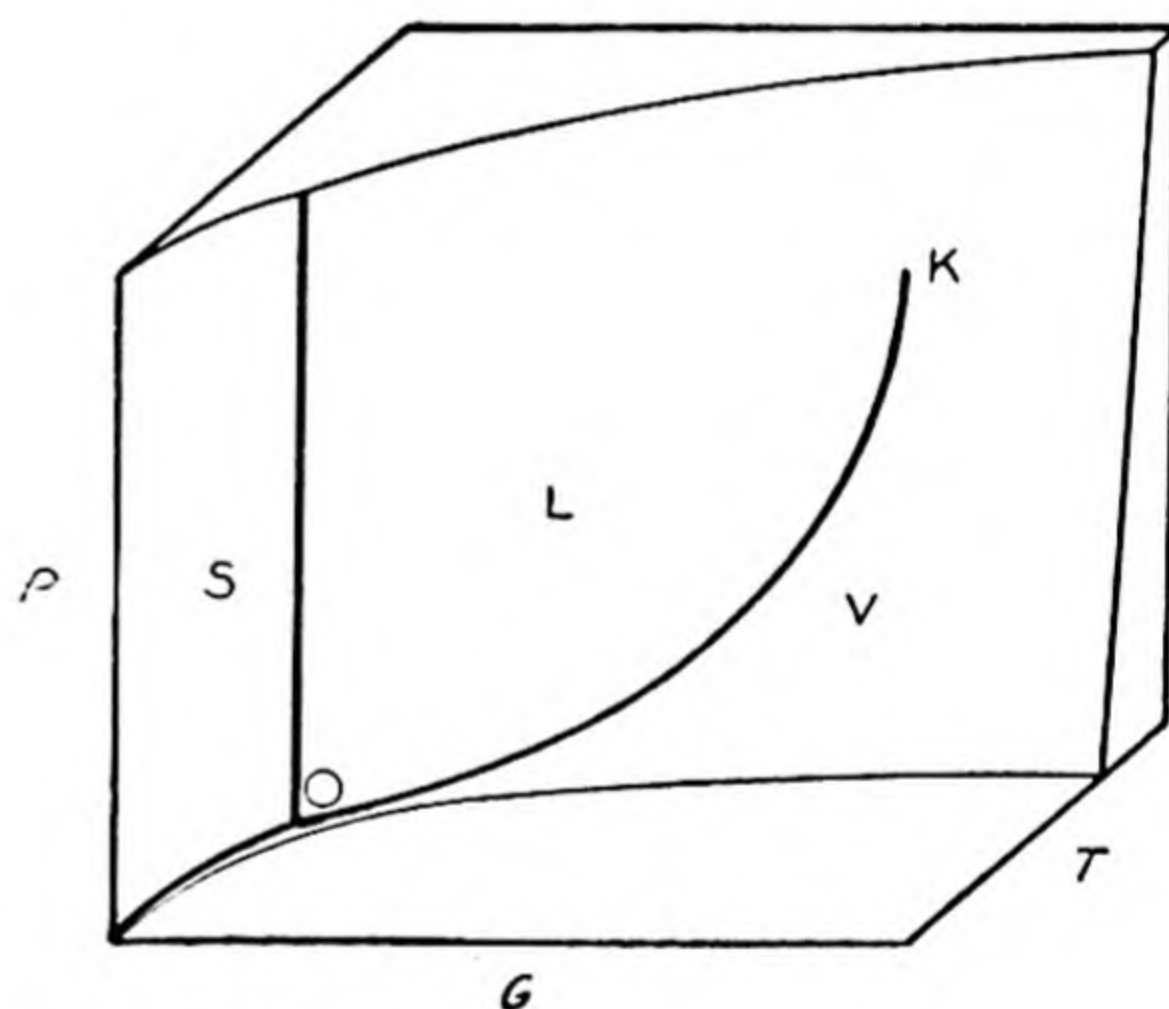


FIG. 2-2. $G/P/T$ diagram for water (schematic).

As stated in Chapter I, this diagram is definitive but not descriptive. Each property, z , of the substance, such as its chemical potential, density, entropy, viscosity, dielectric constant, refractive index, etc., is a function of P and T in each phase. For information about the properties of a particular system, therefore, the phase diagram is to be used in conjunction either with equations (such as an equation of state for the density of the gas phase in terms of P and T) or with 3-dimensional diagrams plotting z , P , and T as coordinates, in which z is one of the properties in question.¹ Of these diagrams, that for the free energy (per mole) or chemical potential (G) (Fig. 2-2) differs from all others in that the value of z is equal in coexisting

¹ For the case of water, see J. C. Slater, *Introduction to Chemical Physics*, McGraw-Hill, N. Y., 1939; pp. 167-173.

phases. All the other plots are of the general form of Fig. 2-3, for the entropy, η ; along a 2-phase curve of the phase diagram, Fig. 2-1, there are here seen to be two discrete values of the property z , one for each phase. At a critical point (K) these two values merge in a continuous curve. At a triple point (O) there are three distinct values, one for each phase. Such plots vary from each other only quantitatively and in respect to the relative position of the three phases (S, L, V in the present case) at a triple point. In Fig. 2-3 the order is SLV since the entropy increases in that order, but in Fig. 2-4, in which the volume V (either specific or molar) is plotted against P and T , for water, the order at the triple point is, of course, LSV.

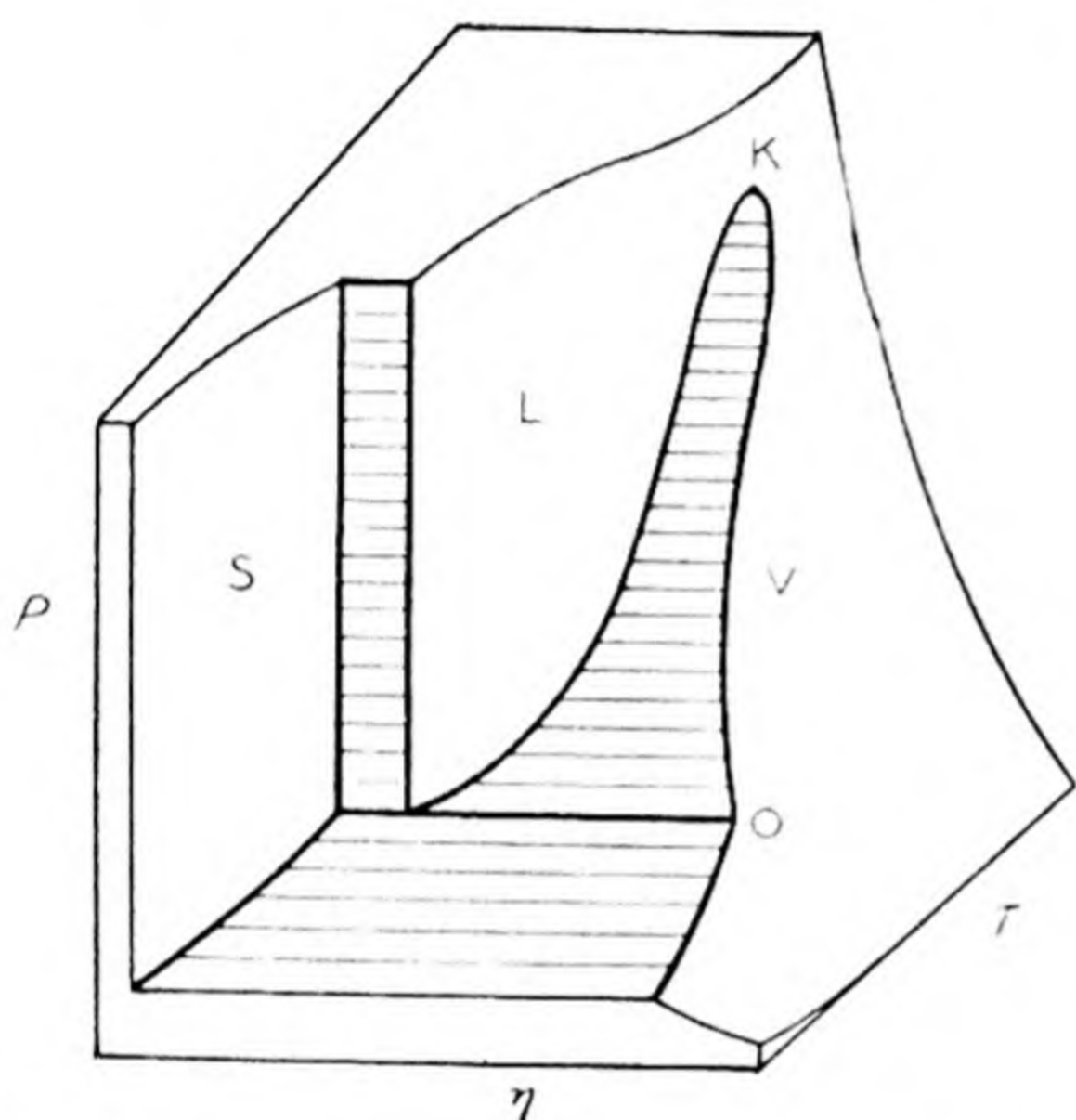


FIG. 2-3. $\eta/P/T$ diagram for water (schematic).

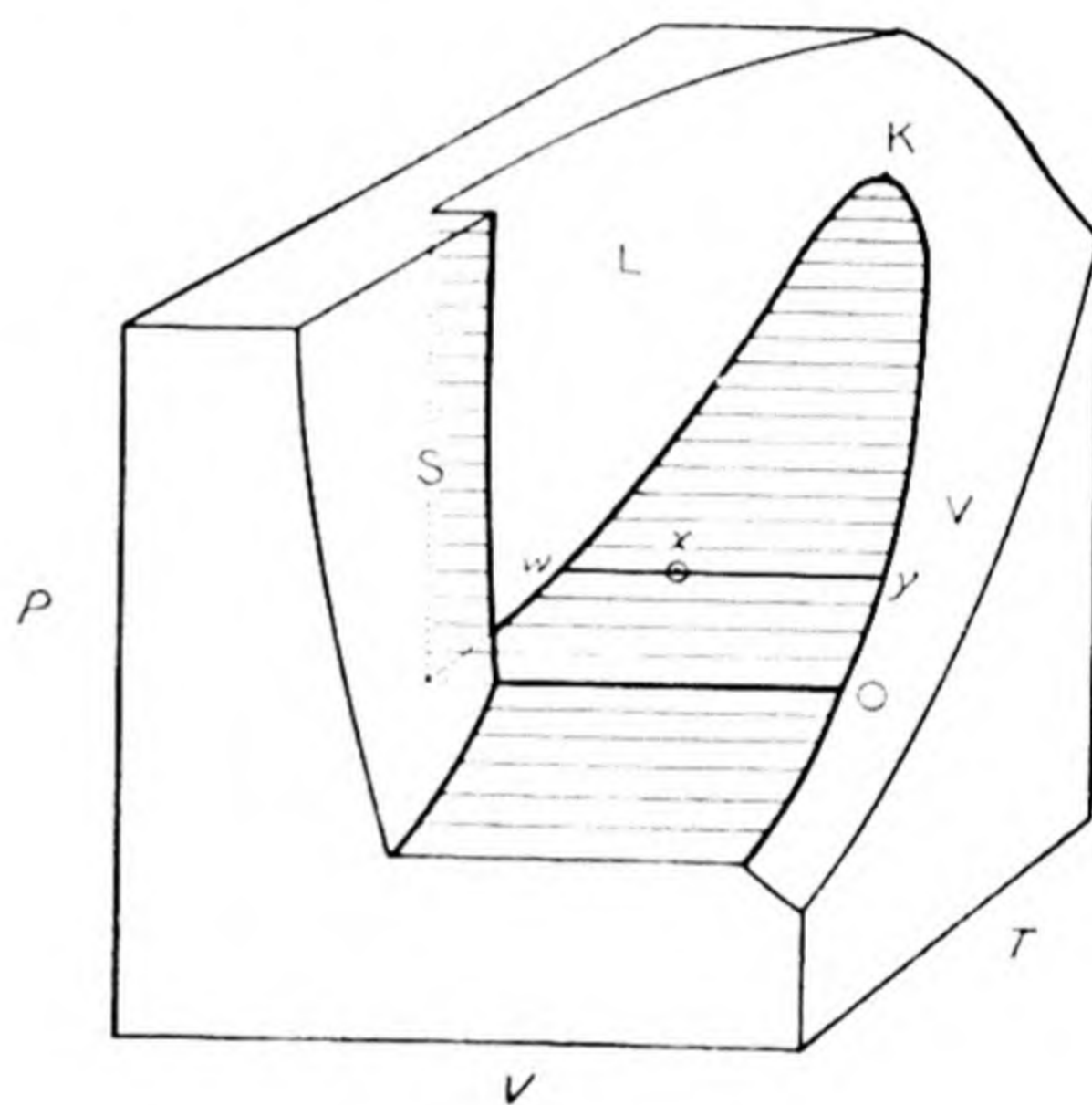


FIG. 2-4. $V/P/T$ diagram for water (schematic).

Fig. 2-4, or the $P/V/T$ diagram, is sometimes discussed as a more complete phase diagram than Fig. 2-1. But the density of a phase is only one of its properties, all of which are functions of the chosen variables P , T . In the $P/V/T$ diagram, as also in one for heat content (volume and heat content both being extensive properties), the tie-lines, isothermal and isobaric, may be used to calculate the relative proportions of the phases along the univariant, 2-phase boundaries of Fig. 2-1. Since the over-all specific volume of a mixture of two phases is the weighted average of the specific volumes of the separate phases, the specific volume of a 2-phase complex falls on a point in an isothermal, isobaric tie-line of Fig. 2-4, such that the segments of the tie-line are inversely proportional to the weights of the respective phases they join. A mixture of L and V with $V = x$, for example, consists of L and V in the weight ratio yx/wx . If Fig. 2-4 is transformed to one of density, pressure, and temperature, then this principle of the "center of gravity" on a 2-phase tie-line gives the relative volumes of the two

phases connected by the tie-line. But the proportions of the three phases at the triple point depend not only on the specific volumes or densities but also on the heat content of the system and on the latent heats of transition.

Tammann² divides the properties of a system into two groups according to whether they change discontinuously or not with the change of state of aggregation, or at a phase transition, essentially the difference between Fig. 2-2 for G , and Figs. 2-3 and 2-4 for η , V , and all other properties. A discontinuity is to be distinguished from a mere break in the curve of the property. Thus if the chemical potential G , or any quantity depending upon it such as the vapor pressure, osmotic pressure, electromotive force (these being measured if necessary in binary or higher systems), in each of two states of aggregation is plotted against T at constant P , or against P at constant T , the two curves cross at a phase transition boundary. The curves of these properties have different slopes in the two states, but the properties have identical values for the two phases at the transition boundary. On the other hand, the curves of the second class of properties, such as density, heat content, electrical conductivity, refractive index, magnetic susceptibility (Tammann also lists the solubility of a foreign gas in the phase), are discontinuous at the point of phase transition. These are the properties used in thermal and dilatometric methods of investigating phase boundaries.

B. Phase Transitions

We return now to the phase diagram, or Fig. 2-1. According to this diagram, if the values of the coordinates P and T are given by point x , the system is a solid, the properties of which are learned from further equations and diagrams, as just explained. If the system is heated at constant P , it remains in one phase S , until the SL phase boundary line (fusion curve) is reached. Here at constant P the temperature remains constant until the solid is completely transformed to liquid, since the system is isobarically invariant while in two phases. The phase transition occurs, of course, in accordance with Le Chatelier's theorem; the heat added is absorbed in transforming the solid to a phase of higher heat content. The diagram gives the temperature at which this transformation occurs, for the arbitrarily chosen P , but not the relative amounts of the phases during the transformation, depending on latent heat and heat content. The temperature rises again only when all the solid is melted, and the system then remains in one phase, L , with rising T , until the LV curve (vaporization

² G. Tammann (Ref. S-1), *Text Book of Metallography*, Chemical Catalog Co., N. Y., 1925; p. 64.

curve) is reached. There again, in two phases, the system maintains constant T (at constant P) while heat is absorbed to vaporize the liquid, until V alone is left. Then the system, in the form of gas, undergoes no further phase transition as T rises at constant P .

A system at point y is entirely gas; if compressed at constant T it remains a gas until the SV (sublimation) curve is reached, where P remains constant while the gas is solidified. Again the transition is according to Le Chatelier's theorem, the change at constant T being to a system of higher density. When all the gas phase is consumed, the system is a solid, during further increase of P , until the fusion curve, SL , is reached; here again P remains constant during melting, the solid being changed at constant P (for constant T) to a phase of still higher density, which is the liquid in the case of water.

Changes under either adiabatic or constant volume (total density) conditions proceed, on the other hand, along the univariant 2-phase curves of the diagram. If heat is added at constant volume to a system consisting of liquid and vapor (that is, one on the LV curve), P and T both rise, while the ratio L/V changes, as may be seen on Fig. 2-4, and the system remains on the LV curve until one of the phases is consumed. Similarly if an SV system is subjected to adiabatic expansion, both P and T fall, along the SV curve, until all the solid is consumed.

If the 3-phase invariant system, point O , is subjected to such changes, it adjusts itself, maintaining constant P and T through phase changes, until one phase is gone, and then proceeds along one of the three univariant curves originating at point O . Adiabatic expansion causes both S and L to vaporize, a process requiring heat; T remains constant therefore as long as there is liquid to be solidified, liberating heat. Hence the system leaves point O when L is consumed and proceeds along the SV curve. Expressed differently, adiabatic expansion leads to a drop in P , and hence the only curve possible on leaving the triple point is SV . Adiabatic compression causes condensation of gas and necessitates liquefaction of solid for invariance. Hence the system leaves point O for either the SL or the LV curve according to its heat content, or according to whether the gas or the solid is first consumed. Changes of heat content at constant volume have effects which vary according to the sign of the slope of the fusion curve. On addition of heat the system must move along a curve on the right of point O , and with removal of heat it must leave O for a curve at lower T . For water, therefore, addition of heat causes vaporization of both L and S , and melting of S to L , processes maintaining invariance by compensation, and finally the solid is all consumed, leaving the equilibrium LV ; subtraction of heat causes the reverse changes, but the system enters either the fusion or the sublimation

curve, depending on whether the gas or the liquid phase is first consumed, or, as in Fig. 2-4, on the volume of the system, whether it is between L and S or between S and V.

C. Phase Transition Curves

The shape and direction of a univariant P/T curve are given by the Clapeyron-Clausius equation,

$$\left(\frac{dP}{dT}\right)_{1 \rightarrow 2} = \frac{\Delta H_{1 \rightarrow 2}}{T(V_2 - V_1)},$$

in which ΔH is the (molar or specific) heat absorbed in the transition of phase 1 to phase 2, and V is the (molar or specific) volume of a phase. ΔH is positive for the transition $S \rightarrow L$, $S \rightarrow V$, $L \rightarrow V$. Hence both the sublimation and the vaporization curves have positive slopes, since $V_2 - V_1$ is in each case positive. At any given T , however, the sublimation curve is steeper than the vaporization curve, since $\Delta H_{S \rightarrow V} = \Delta H_{S \rightarrow L} + \Delta H_{L \rightarrow V}$, and they intersect at the triple point O. As for the fusion curve, the melting point is seen to be raised (positive slope) by P , if the solid is denser than the liquid; a negative slope is found in those few cases (water, bismuth, gallium) where the liquid is denser than the solid. Even in these unusual cases, however, it is found that at still higher P there is always some change in the slope of the fusion curve, as the result of (high pressure) polymorphism of the solid, and the general tendency of all systems is to have a positive slope of the fusion curve, the average value, as observed by Bridgman,³ being ~ 60 atm/degree. According to Slater⁴ the positive slope is to be expected since with $dP/dT = (\Delta H/T)/\Delta V$, the entropy change, $\Delta H/T$, and the volume change, ΔV , will tend to have the same sign; and on the basis of average specific heats and densities of solids and liquids, an approximate slope of 50 may be predicted.

Despite the general positive slope ultimately attained by the fusion curve, a critical point of identity of the S and L phases, similar to point K for the L and V phases, seems to be impossible. While the difference between L and V may be considered one of degree, that between S and L is one of quality, involving order and arrangement, so that apparently the transition entropy can never become zero. Actually, no indication of such a critical point has ever been found, nor is there any indication of such increasing similarity between the solid and liquid phases, with increasing P and T , as to lead one to expect their ultimate coalescence at a critical point.⁵

³ P. W. Bridgman, *Proc. Amer. Acad.*, **72**, 45 (1937).

⁴ J. C. Slater, *loc. cit.*, p. 220.

⁵ P. W. Bridgman, *Proc. Amer. Acad.*, **47**, 441 (1912).

The continued positive slope of the fusion curve, observed even at the highest pressures used (Bridgman; $> 40,000 \text{ kg/cm}^2$ at 200°C), fails to give support ⁵ to the theoretical prediction of Tammann ⁶ that the SL curve should bend back upon itself in its course from the triple point O, passing first through a T -maximum corresponding to the condition of equal densities for the two phases, and then through a P -maximum, corresponding to the condition of equal values of the heat content.

The critical point ending the LV curve, on the other hand, is expected on the basis of the disordered nature of the phases involved, and equations of state, involving the relation between these phases, may be used to calculate the constants of the system at point K. The only line leading to point K, on the P/T diagram, is the LV or vaporization curve; a horizontal division between L and V fields, by a line between the fusion curve and point K, frequently shown on such a diagram, has no strict meaning. The distinction between the L and V phases has meaning only on the LV curve itself. The "liquid" at point x' can be "transformed" to the "gas" at point x'' without phase transitions, by varying P and T so as to pass above and around point K. Furthermore, a sample of the system in a closed vessel (constant volume) held originally at some value of T above T_K , will show, upon cooling, the critical phenomenon (appearance of identical L and V phases in equal amounts) only if the density of the system is the critical density; it otherwise passes above or below point K. With higher density, no phase transition is observed until either the SL or the LV curve (from above) is reached, at $T < T_K$; if the density is too low, the system similarly remains a single phase until it reaches either the LV curve (from below, giving a non-critical condensation, or dew-point phenomenon) or the SV curve. In reverse, an enclosed sample of L + V will show the critical phenomenon (disappearance of a median meniscus) only if the density is the critical density; if the density is too high the meniscus disappears at the top of the tube — disappearance of gas — and if too low, it disappears at the bottom — disappearance of liquid (cf. Fig. 2-4). In any case, if the sample does not have the correct density the meniscus always appears or disappears at a temperature below the critical.⁷

D. Triple Points

The relative configuration of three univariant curves meeting at a triple point is fixed by two principles. The first is the Clapeyron-Clausius equation determining the slope of each curve, according to which isothermal

⁶ *Loc. cit.* (Ref. S-1), p. 34.

⁷ For an example of these relations in the determination of the critical point of (nitromethane) see D. N. Griffin, *J. Am. Chem. Soc.*, **71**, 1423 (1949).

increase of P must cause transition to forms of higher density while isobaric increase of T must cause transition to phases of higher heat content. The other is that the (metastable) extension of each curve beyond the triple point must lie between the other two stable curves. When a metastable univariant 2-phase system persists beyond (in respect to P and T) the triple point, it is unstable in respect to the third phase; and if the metastability is removed, at constant P and T , the system consists entirely of the single new phase.

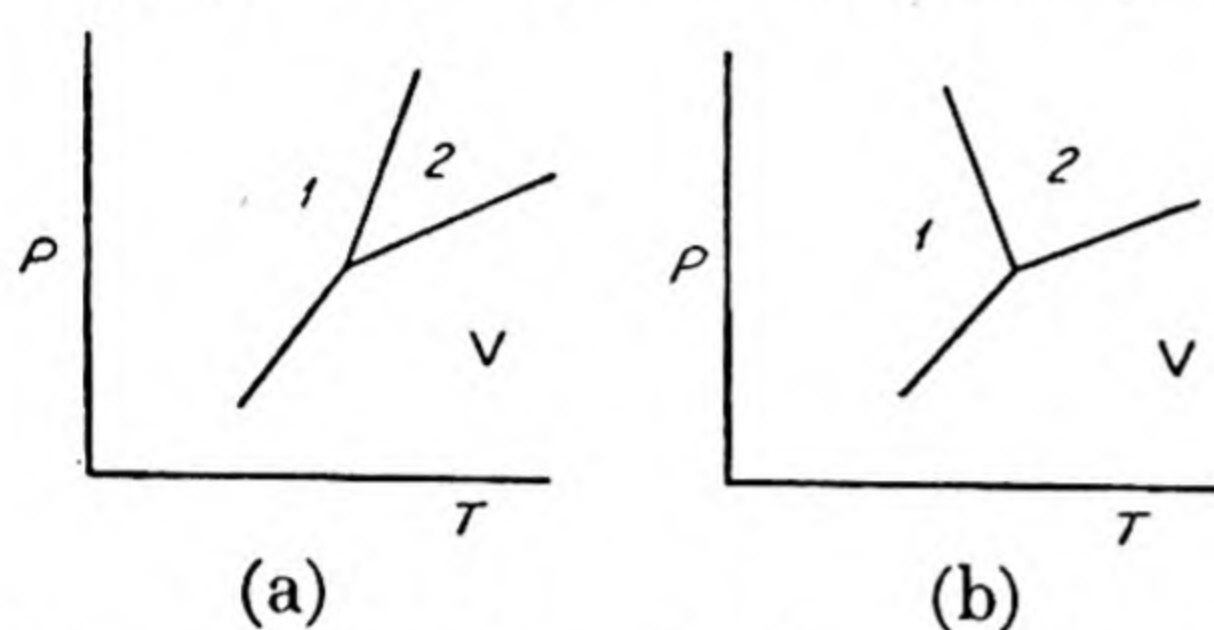


FIG. 2-5. Triple points involving the vapor phase, V.

the higher heat content. If all three phases are condensed phases, the only requirement is that the metastable extensions lie between the other two stable curves, with the slope of each curve determined by the Clapeyron-Clausius equation. If L is involved, the change $S \rightarrow L$ must occur with rising T at constant P .

A metastable equilibrium state, such as the metastable 2-phase system represented by the extension dO of the LV curve of Fig. 2-1 beyond the triple point, or supercooled liquid water, is a state of higher free energy than that of the system in the stable form for the given P and T . This is not to be seen from the P/T diagram but it could be seen from Fig. 2-2. Hence the pressure of a metastable system involving a gas phase is always higher than that of a more stable system involving V, at the same T ; the extension of the sublimation curve lies above the stable LV curve, and the extension of the LV curve, or supercooled liquid in metastable equilibrium with vapor, lies above the stable SV curve. If the triple point is one involving two solids and vapor, therefore, it follows that at the same T , the metastable solid has the higher chemical potential, and hence the higher value of any intensive property depending on the chemical potential, such as vapor pressure and solubility. Such triple points therefore may be fixed in two general ways. The first is as points of invariance in respect to P and T while the system consists of three coexisting phases, as in cooling curves. The second is as the intersection of two univariant curves, P/T transition curves in the study of high pressure phenomena, or (for the temperature, at least, of the triple point) as the intersection of curves plotting an intensive property (vapor pressure, solubility in a foreign solvent, E.M.F. of cells) against T .

Finally, if the metastable curves around a triple point are included, either an isotherm or an isobar (straight line changes on the diagram) cuts three univariant curves, on either side of the triple point. This is an important principle, later extended to the P/T relations of a binary system. In the case of point O of Fig. 2-1, for example, an isobar at $P > P_o$ crosses, successively, the stable SL, the metastable SV, and the stable LV curve, while at $P < P_o$ it cuts successively the metastable LV, the stable SV, and then the metastable SL curve. In either case the middle curve crossed by the isobar is the equilibrium, stable or metastable, between phases related by the greatest heat of transition, always SV; but the middle curve crossed by an isotherm is the equilibrium between phases of greatest difference in density, SV or LV, not SL.

E. True and Normal Transition Points

The temperature of the SLV triple point of a system such as water is that of the equilibrium ice + liquid + vapor at a pressure fixed by the system itself, close to 4.58 mm. By "the pressure of the system" is meant a total P equal to the vapor pressure of the system. "A system under its own P " or "under the vapor pressure," therefore, means one with a vapor phase present, even if this vapor phase is ignored in representation. But "high pressure phenomena" will mean equilibria between condensed phases at pressures not allowing the existence of a vapor. When the temperature of the 3-phase equilibrium is measured in open air, the observed T differs from that of point O for more than one reason. If the air is in solubility equilibrium with the water, the system is binary (counting the air as a single component); if it is not, the air may be considered as acting as a mechanical gas piston, merely lowering the fusion temperature in accordance with the Clapeyron-Clausius equation and, to a negligible degree, raising the vapor pressure p of the water in accordance with the Gibbs equation, $(dp/dP)_T = \bar{v}_L/\bar{v}_V$ (\bar{v} being the specific volume). The reference point of thermometry, 0°C , is defined as the normal melting point of water in equilibrium with air, the total pressure being one atmosphere. This is found to be 0.0024° below the normal melting point of pure water, that is, in air, at $P = 1$ atmosphere, but with no air in solution. Pure water, in other words, under a total gas pressure (mechanical gas piston) of 1 atmosphere freezes at $+0.0024^\circ\text{C}$, and it is this temperature that has to be corrected to 4.6 mm to give the temperature of the triple point. The correction, given by the Clapeyron-Clausius equation, being $+0.0074^\circ$, the triple point is at $+0.0098^\circ$ and 4.58 mm.⁸ The triple point in air, then, varies with the

⁸ W. Waring, *Science*, **97**, 221 (1913). More recently the temperature of the triple point has been revised to $+0.0100^\circ$; H. F. Stimson, *J. Res. Natl. Bu. Standards*, **42**, 209 (1919), Res. Paper 1962.

atmospheric pressure and lies on the SL curve of Fig. 2-1 if the air is insoluble in water, but the binary triple point, with air saturating the water, and at $P = 1$ atm, lies on a different curve, one in the three dimensions P, T, c , the projection of which would appear slightly on the left of SL, but still originating from O.

A "normal" transition point, then, either of melting or of boiling, if it refers to a determination under one atmosphere of pressure of actual air, may have two meanings, depending on whether or not the substance is saturated with the air; for most purposes the difference caused by dissolved air is, of course, negligible.

Since no substance is known with $P_K < 1$ atm, we may say that every substance (the only known exception being helium) has either both a normal melting point and a normal boiling point (if P_O is < 1 atm, as in the case of water, iodine, and perhaps the majority of familiar substances) or only a normal sublimation point (if P_O is > 1 atm, as in CO_2). If, as in the case of iodine, Fig. 2-6, the vapor pressure of the solid (the SV curve)

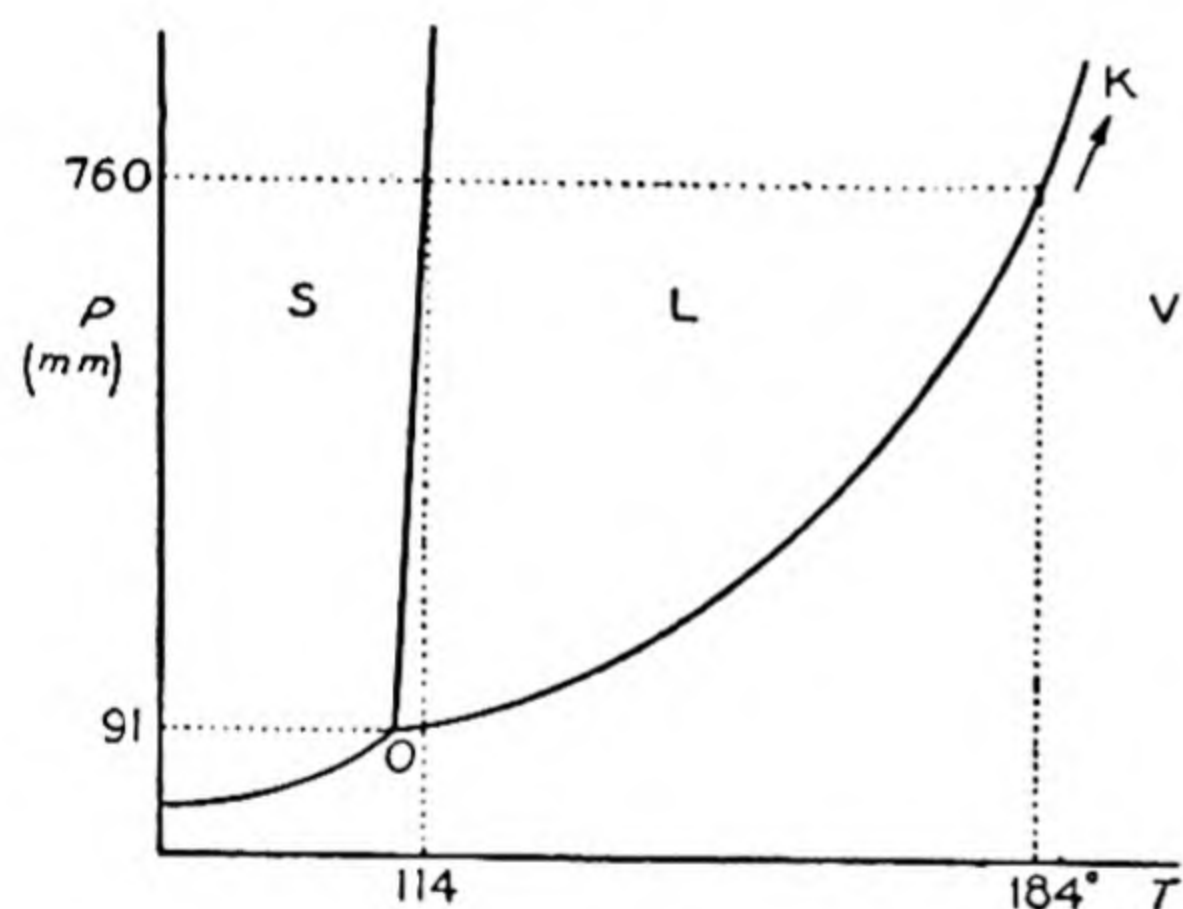


FIG. 2-6. Iodine diagram (schematic).

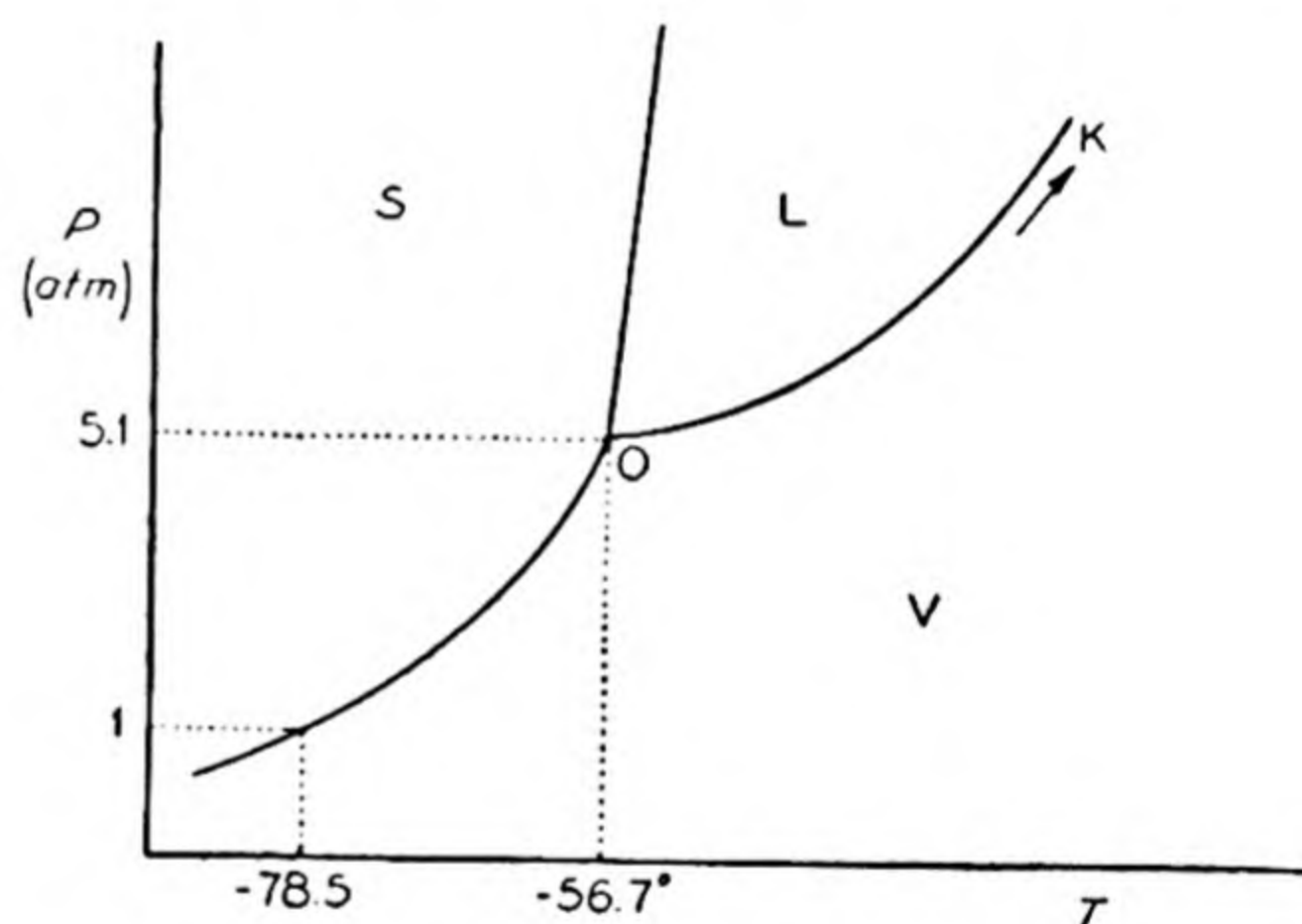


FIG. 2-7. Carbon dioxide diagram (schematic).

is somewhat high, but < 1 atm at the triple point, the substance may be said to be (practically) sublimable, but it does not have a normal sublimation point. The difference between iodine and water is, therefore, only one of degree in this respect. If a small amount of iodine is heated in the open, in a shallow container, it may be completely vaporized before reaching its melting point. (In Fig. 2-6 the normal melting point is 114, the normal boiling point 184°; K is at 553°.) But in the case of CO_2 , Fig. 2-7, which has a normal sublimation point (at -78.5°) but not a normal boiling point, the liquid state is obtainable only with values of P and T falling in the L field, and therefore at $P > 1$ atm and not in the open air; K for Fig. 2-7 is at 31.1° and 73 atm pressure.

Any one of the three "normal transition points" may be used as a source of constant T in the open air, for, provided the substance is either always saturated with air or pure throughout, the equilibrium will be an invariant one. Solid CO_2 , in equilibrium with its vapor at the constant pressure of 1 atm, will evaporate at constant T (-78.5°) until the solid is all consumed. Similarly liquid water, boiling at 1 atm P , that is, in equilibrium with its vapor at the constant pressure of 1 atm, will evaporate at the constant T of 100° until the liquid is all consumed. The normal melting point, as a 3-phase equilibrium in open air at constant P , is, of course, also invariant.

F. Polymorphism (Allotropy)

If a substance can exist, stably or metastably, in a greater number of condensed forms than the two represented by the minimum of a single solid and a single liquid, we may call it **polymorphic**, possessing polymorphic or allotropic forms. The existence of two liquid forms is known only in the case of helium. Furthermore, those forms known as liquid crystals or crystalline liquids are usually called mesomorphic forms. But the P/T relations of such forms are the same as for those commonly recognized as definite polymorphic crystalline varieties of a substance. As the number of possible phases increases above the three fundamental forms of S, L, V, additional lines and triple points may appear on the P/T diagram. If the number of phases is n , the number of geometrically possible (but not necessarily realizable with positive values of P and T) 2-phase lines is $\sum_n (n-1)$, and the number of geometrically possible 3-phase points^{8a} is $n(n-1)(n-2)/3!$. Polymorphism of the solid state occurs not only at ordinary pressures but also commonly at high pressure.

1. Enantiotropy

Let us consider a system forming four phases: S_α , S_β , L, V, in which S_β is assumed to have a higher heat content than S_α , and is known as the high temperature form. S_β may be either a second solid form or a mesomorphic phase, intermediate between a true solid and a true (isotropic) liquid. The four "possible" triple points are now usually $S_\alpha S_\beta V(T_1)$, $S_\alpha LV(T_2)$, $S_\beta LV(T_3)$, and $S_\alpha S_\beta L(T_4)$. The first (T_1) is commonly called *the* transition point of the substance, the next two are melting points, and the last is a condensed transition point. If both S_α and S_β can exist in stable equilibrium with vapor, the relation is called enantiotropy, and the transition point

^{8a} E. Riecke, *Z. phys. Chem.*, **6**, 411 (1890).

values at the triple points: 95.5° (0.007 mm) at T_1 , for $S_R S_M V$; 112.8° at T_2 , for $S_R LV$; 119.2° (0.05 mm) at T_3 , for $S_M LV$; 151° (1320 kg/cm²) at T_4 , for $S_R S_M L$.⁹

When several successive forms are possible, all capable of existing in stable equilibrium with the vapor, the P/T diagram simply shows a succession of transition points of the type T_1 , and of transition curves of the type $S_\alpha S_\beta$. An example is ammonium nitrate¹⁰ (Fig. 2-10, schematic), the temperatures being: T_α , -18° ; T_β , $+32^\circ$; T_4 , 64° (830 kg/cm²); T_γ , $83-84^\circ$; T_δ , 125° ; T_ϵ , the melting point, 169° . The numerous mesomorphic states observed for sodium soaps would also be of this class. The successive forms of sodium palmitate, for example, are: crystalline solid ("curd fibers"), subwaxy, waxy, superwaxy, subneat, neat soap, and isotropic (true) liquid. Homologous soaps show, moreover, as expected, parallel polymorphism,¹¹ and when the temperatures of the corresponding transition points are plotted against the number of carbon atoms in the acid radical of the soap, they show a tendency to converge with increasing length of the carbon chain, on the basis of which it might be expected that ultimately the only transition left would be the over-all change from true solid to true liquid.¹² The temperature of this ultimate, common transition would presumably be $\sim 117^\circ$, the "genotypic point" approached with increasing chain length according to the "law of convergence" of Timmermans.¹³

In the case of iron there are two enantiotropic transition points below the melting point, with the sequence α -Fe (to 900° , T_1), γ -Fe (to 1400° , T'_1) and δ -Fe (to the melting point, 1530° , T_3). A magnetic, second-order, transition occurs at 770° , so that the iron between 770° and 900° was once called β -Fe; but the second-order transition is not a phase change and has no effect on phase diagrams. Moreover, however, it seems that the α and the δ "forms" are actually portions of the same body-centered cubic phase

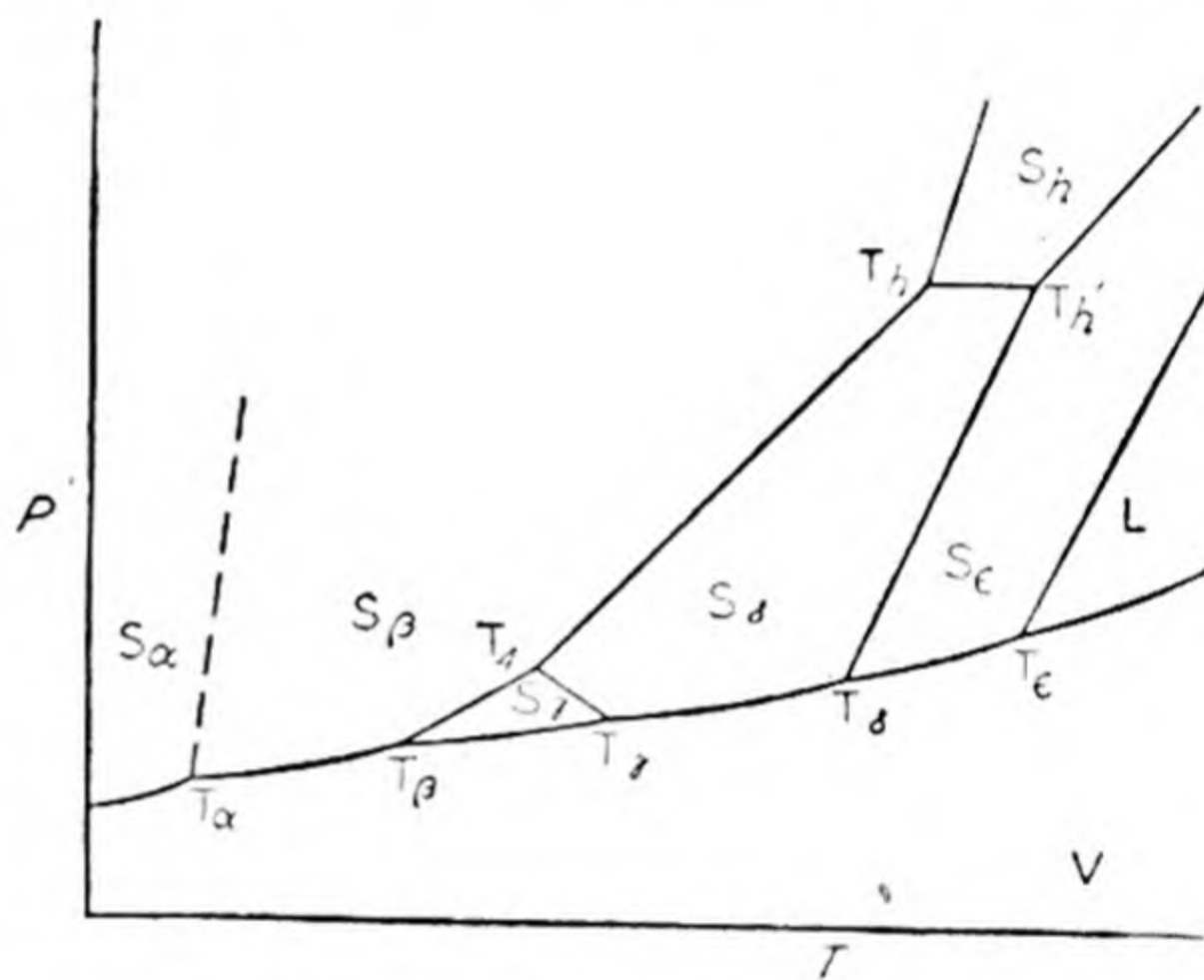


FIG. 2-10. Ammonium nitrate diagram (schematic).

⁹ I. C. T. (*International Critical Tables*, McGraw-Hill, N. Y., 1926), III-201, 202; IV-11. Also A. N. Winchell, *Microscopic Characters of Artificial Minerals*, Wiley, N. Y., 1931; p. 153.

¹⁰ I. C. T., IV-11; Winchell, 209.

¹¹ M. J. Vold, *J. Am. Chem. Soc.*, **63**, 161 (1941).

¹² M. J. Vold, M. Macomber, and R. D. Vold, *ibid.*, **63**, 168 (1941).

¹³ J. Timmermans, *Bull. soc. chim. Belg.*, **28**, 392 (1919).

merely separated over a range of conditions, by the face-centered cubic γ -Fe; a similar relation exists in the case of cobalt.¹⁴ The identity of α -Fe and δ -Fe is based not only on structural properties but also on the continuity of the two forms as a single phase observed in binary systems with a number of alloying elements (cf. Chapter VI). In this case, then, if there are only four actual possible phases of pure iron, one possibility for the phase diagram, still showing only four triple points, is the schematic one of Fig. 2-11, in which the γ -Fe field is closed by a continuous transition curve in the solid area, joining the two enantiotropic transition points T_1 and T'_1 .¹⁵

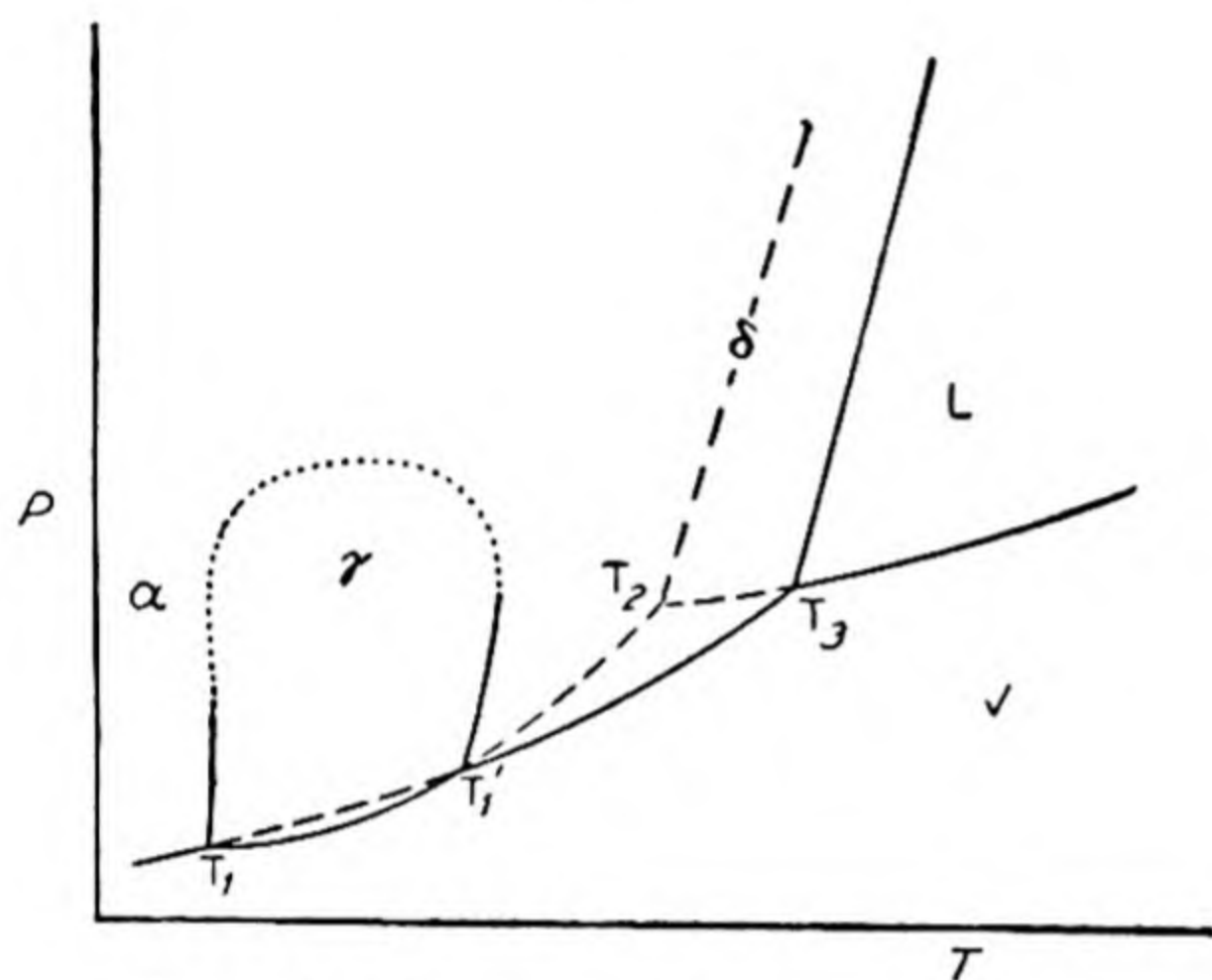


FIG. 2-11. Iron diagram, hypothetical.

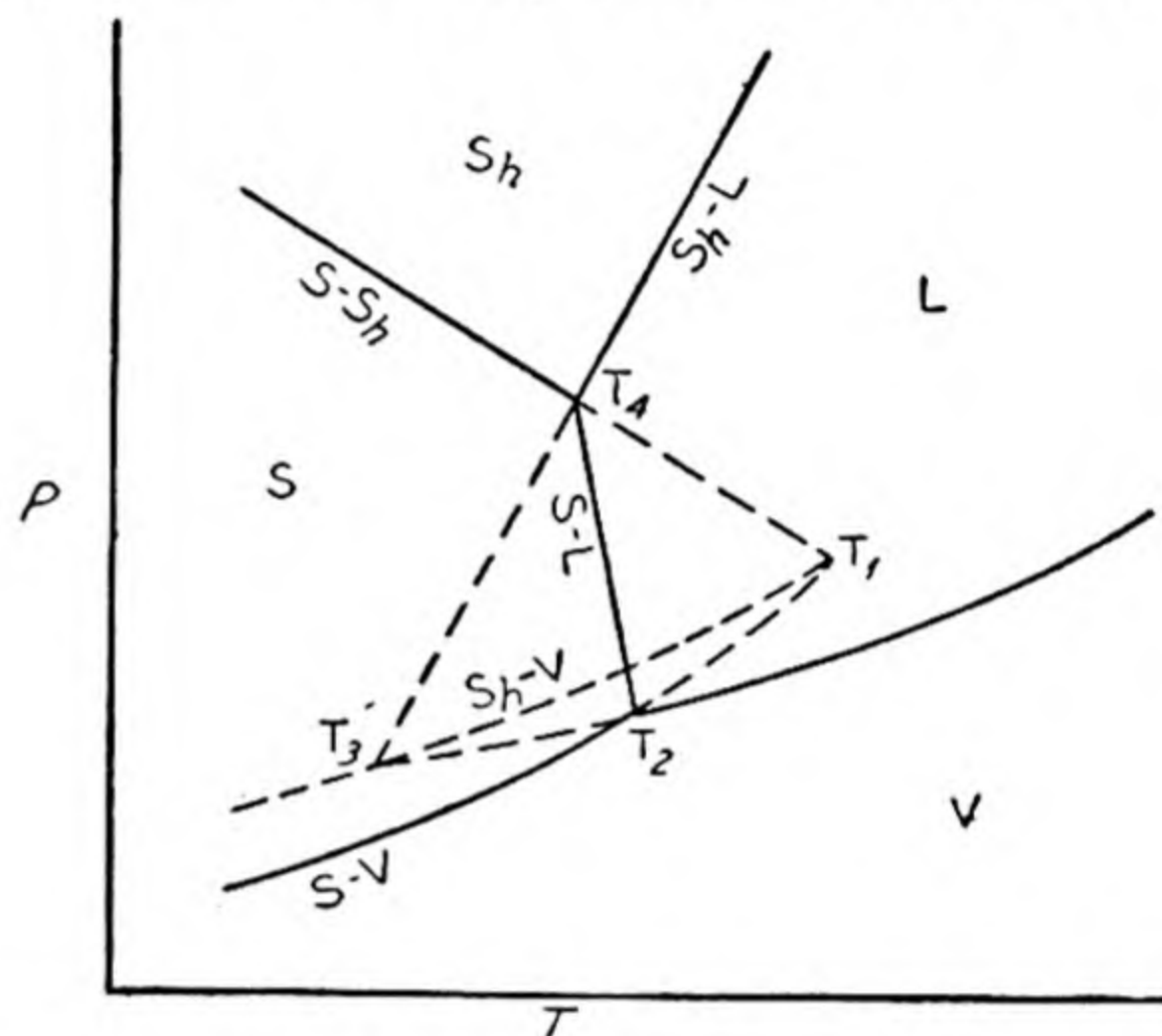


FIG. 2-12. High pressure polymorphism.

2. High Pressure Polymorphism

The substance may have a high pressure form, S_h , appearing as a stable form only at high P , in equilibria not involving the vapor phase. S and S_h of Fig. 2-12, for example, may be taken as referring to ice I and ice III respectively, for water. Now there are, as in Fig. 2-9, only two stable triple points, the melting point of $S(T_2)$ and the condensed transition point $SS_hL(T_4)$. The "melting point" of $S_h(T_3)$ or the triple point S_hLV , is metastable, and conceivably realizable, as by the supercooling of the liquid below T_2 ; but the triple point T_1 for the phases SS_hV , the "transition point" at the pressure of the system, is unrealizable. Many examples of this type of polymorphism (high pressure) have been studied, particularly by Bridgman and by Tammann. The most interesting example is that of water, in which seven different crystalline forms have been noted, Fig. 2-13. The coordinates of the various points for the P/T diagrams of the separate systems ordinary water and D_2O are as follows:^{5, 16}

¹⁴ F. Seitz, *The Modern Theory of Solids*, McGraw-Hill, N. Y., 1940; pp. 8, 487.

¹⁵ Cf. the figure on p. 34 in Tammann (Ref. S-2), *States of Aggregation*, D. Van Nostrand, N. Y., 1925.

¹⁶ P. W. Bridgman, *J. Chem. Physics*, **3**, 597 (1935); **5**, 964 (1937).

Points	Phases	Water		D ₂ O	
		$T, ^\circ\text{C}$	$P, \text{kg/cm}^2$	$T, ^\circ\text{C}$	$P, \text{kg/cm}^2$
a	ice I, ice III, L	- 22.0	2115	- 18.75	2245
b	ice III, ice V, L	- 17.0	3530	- 14.5	3555
c	ice I, ice II, ice III	- 34.7	2170	- 31.0	2290
d	ice II, ice III, ice V	- 24.3	3510	- 21.5	3540
e	ice V, ice VI, L	0.16	6380	+ 2.6	6405
f	ice VI, ice VII, L	81.6	22,400		
g	ice IV, ice V, L			- 6.2	5410

Ice V is presumably stable between b and e , and point g is a metastable point involving the phases ice IV, ice V, L. The points T_h and T'_h of Fig. 2-10 are, of course, similar high pressure triple points, the first at 169° and 8870 atm, the second at 187° and 8730 atm.

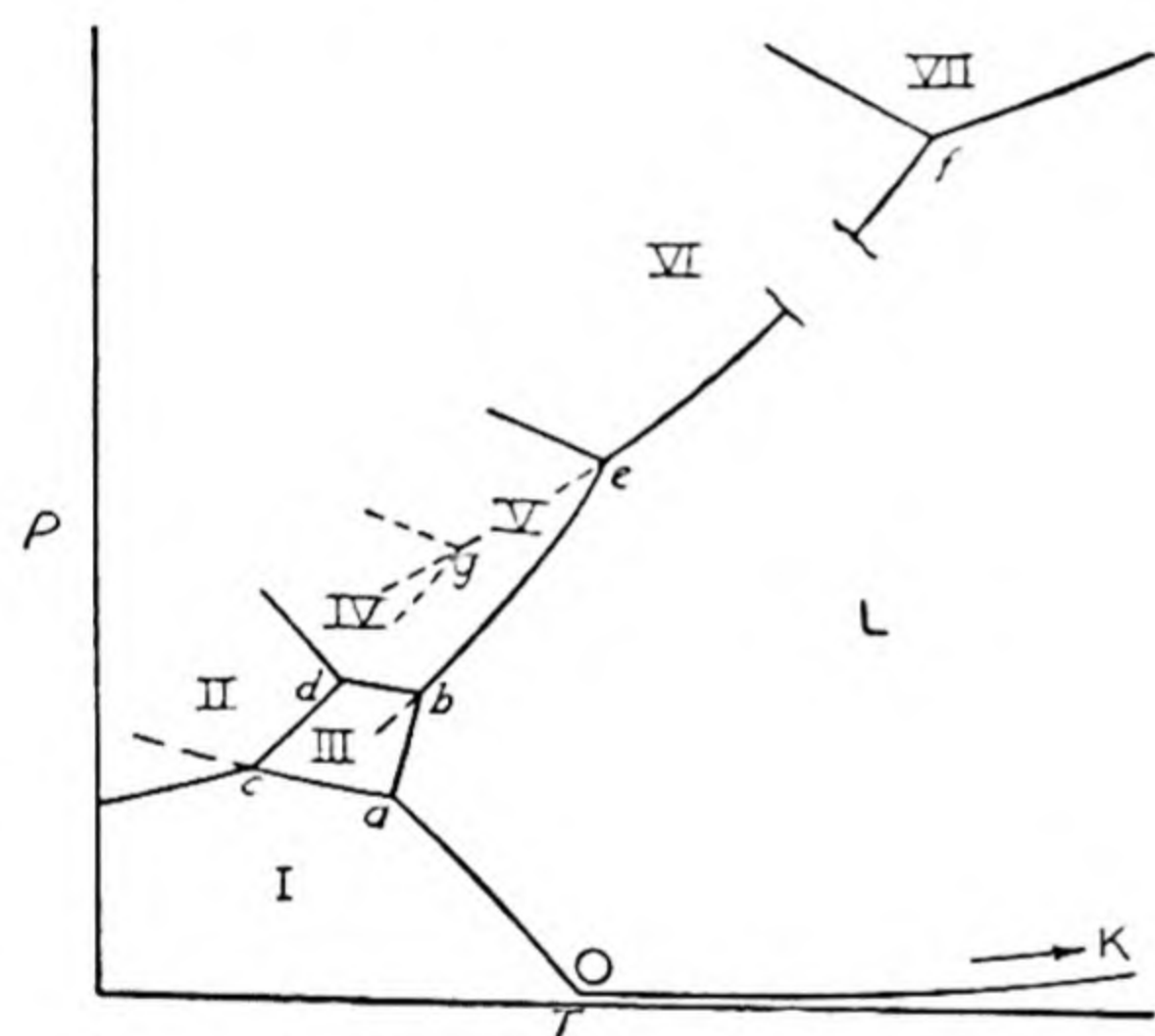


FIG. 2-13. High pressure polymorphism of water (schematic).

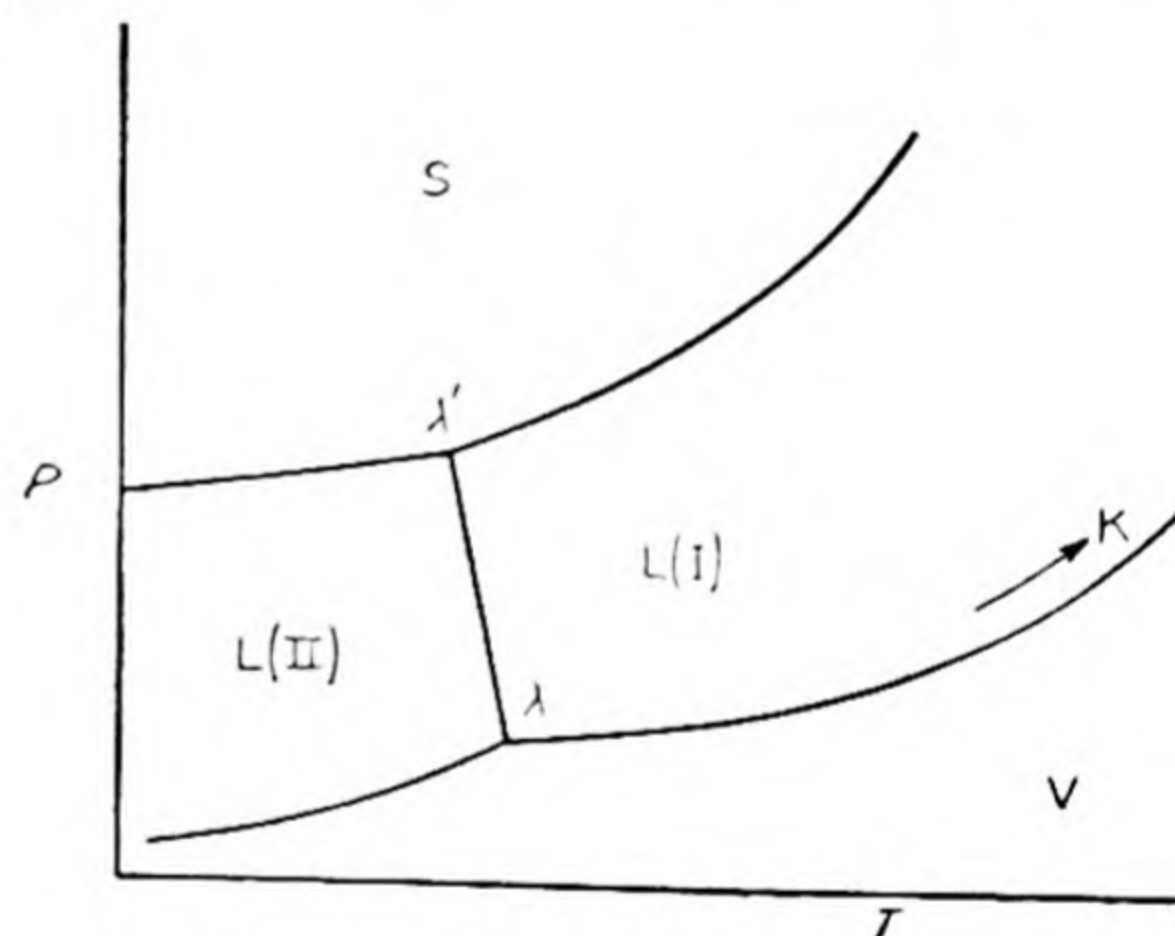


FIG. 2-14. Helium diagram (schematic).

Under this type we may also include helium, with its two liquid forms, L(I) and L(II), and with a solid obtainable only in equilibrium with condensed phases, Fig. 2-14 (schematic). The system is noteworthy not only because of its two liquid forms and their remarkable properties but also for the extraordinarily low slope of the SL(II) curve, which reflects the very small difference in entropy between these two phases. The triple point L(II)L(I)V is referred to as the λ -point (2.19°K , 38.3 mm); the temperature of the condensed transition, L(II)L(I), is then lowered by increasing P to 1.78°K and 30.0 atm (point λ'), where solid appears. Thus mere cooling does not solidify the liquid, except under pressure; there is no triple point involving both S and V. The critical point K occurs at 5.2° absolute and 2.26 atm.¹⁷

¹⁷ W. H. Keesom, *Helium*, Elsevier, Amsterdam, 1942; p. 226.

3. Delayed Transformation; Glass

In some cases a solid form cooled below its transition temperature, and hence metastable, may possess so high a degree of practical stability as to reveal further enantiotropic variations on the metastable level. An example of persistent metastability of polymorphic modifications is found in the silica system. The stable forms, presumably each in equilibrium with vapor, are, with increasing T , α -quartz to 575° , β -quartz to 870° , β_2 -tridymite to 1470° , β -cristobalite to 1710° , the melting point.¹⁸

All these transformations, however, are slow. In the first place the liquid is very easily supercooled, and because of the crystallographic requirements for the arrangement of a true crystal, and the high viscosity soon attained through some cooling below the melting point, the material persists almost indefinitely in what is called the glassy or vitreous condition. The actual internal structure, and hence all the properties, of this unstable material will depend on the history, that is, the length of time it is kept at any particular temperature during cooling, from the melting point down to room temperature. The situation then is not the same as that in the mere metastable supercooling of a liquid, as on curve dO of Fig. 2-1. The latter is a reversible system, with a vapor pressure dependent on T alone, and merely metastable in respect to the solid phase. Silica glass, on the other hand, does not represent simply the metastable extension of the LV equilibrium curve below the melting point. Its vapor pressure, which must depend on the internal structure of the glass, will be a function of its history — age and treatment. Although apparently or physically still a single phase, it is strictly neither a supercooled liquid nor a true solid; it is in fact not a “phase” at all since it is not in reversible equilibrium with any other phase. This is the distinction between “supercooled liquids” or even “supercooled liquids of extremely high viscosity” and the vitreous materials called glasses or amorphous solids. The first term should be reserved for true, reversible though metastable LV systems. The second group consists of materials which cannot be handled by the Phase Rule. They are in the process of transformation, and not at equilibrium, either metastable or stable. This transformation is called devitrification, and it is merely the process of crystallization, or the formation ultimately of one of the stable solids already mentioned, depending on the temperature. The process is accelerated by “working,” or manipulation at high temperature.

The fact that such materials are not subject to the Phase Rule constitutes

¹⁸ This nomenclature may not agree with all the literature, but we shall use the letters α , β , γ , etc. to indicate the order of forms appearing with increasing temperature. See Winchell, *loc. cit.*, p. 191; *I. C. T.*, IV, p. 20.

a great limitation in the applicability of the Phase Rule, since these materials are numerous and important. But it must simply be kept in mind that the Phase Rule applies only to systems in states of reversible heterogeneous equilibrium, and not at all to systems in course of transformation, regardless of the slowness of this transformation. In these cases, then, the glasses, we must speak of slow or retarded transformation, as distinct from metastability.

Silica shows both phenomena to a marked degree. Besides the slowness with which the liquid passes into any true crystalline state, each of the crystalline forms shows marked tendency to persist metastably below its transition point. Thus β -cristobalite, metastable below 1470° , shows an enantiotropic transformation to α -cristobalite at $\sim 220^\circ$; and β_2 -tridymite, metastable below 870° , has enantiotropic transitions to β_1 -tridymite at 163° and then to α -tridymite at 117° . But these forms are all metastable with respect to α -quartz, below 575° .¹⁸

The glassy condition is often very prominent even in binary and higher systems, both in organic and in inorganic substances. When it occurs, it simply sets a limit to the Phase Rule investigation of the system and will for that reason not be considered further.

4. Monotropy

Finally, there is a relation known as monotropy, in which the second form, S' , has or appears to have no region of stability anywhere on the P/T diagram, so that it is always metastable with respect to the stable form S . Such a monotropic form must therefore be obtainable only from a metastable vapor or from a metastable (supercooled) liquid. Thus white phosphorus, which is monotropic in respect to red phosphorus, forms by condensation of the vapor. It has its own melting point; and one interpretation of the allotropy of phosphorus assumes that the LV equilibrium of white phosphorus is continuous with the metastable extension of the LV system produced, at high P , from red phosphorus. Actually this high temperature-high pressure liquid can be supercooled below the triple point of red phosphorus (SLV), but before it can crystallize to the monotropic white phosphorus it always crystallizes to red phosphorus, while from the other end the white form changes rapidly to the red as the temperature is raised, so that there is experimentally a gap in the supposedly continuous LV curve. The assumed relation is, in general at least, a possible one, although because of the internal complexity of phosphorus (its pseudobinary and pseudoternary behavior) the two LV curves may pertain to liquids of different internal constitution and hence to different "Systems."

In monotropy, then, the melting point T_3 of the metastable (monotropic)

form is metastable and below (in P and T) the stable melting point of the stable form (T_2), the liquid being assumed the same (in internal constitution) for both triple points. It is then further assumed that the "transition point," $SS'V(T_1)$, is now above the melting point of S , as in Fig. 2-15, so that we distinguish enantiotropy from monotropy in that the transition

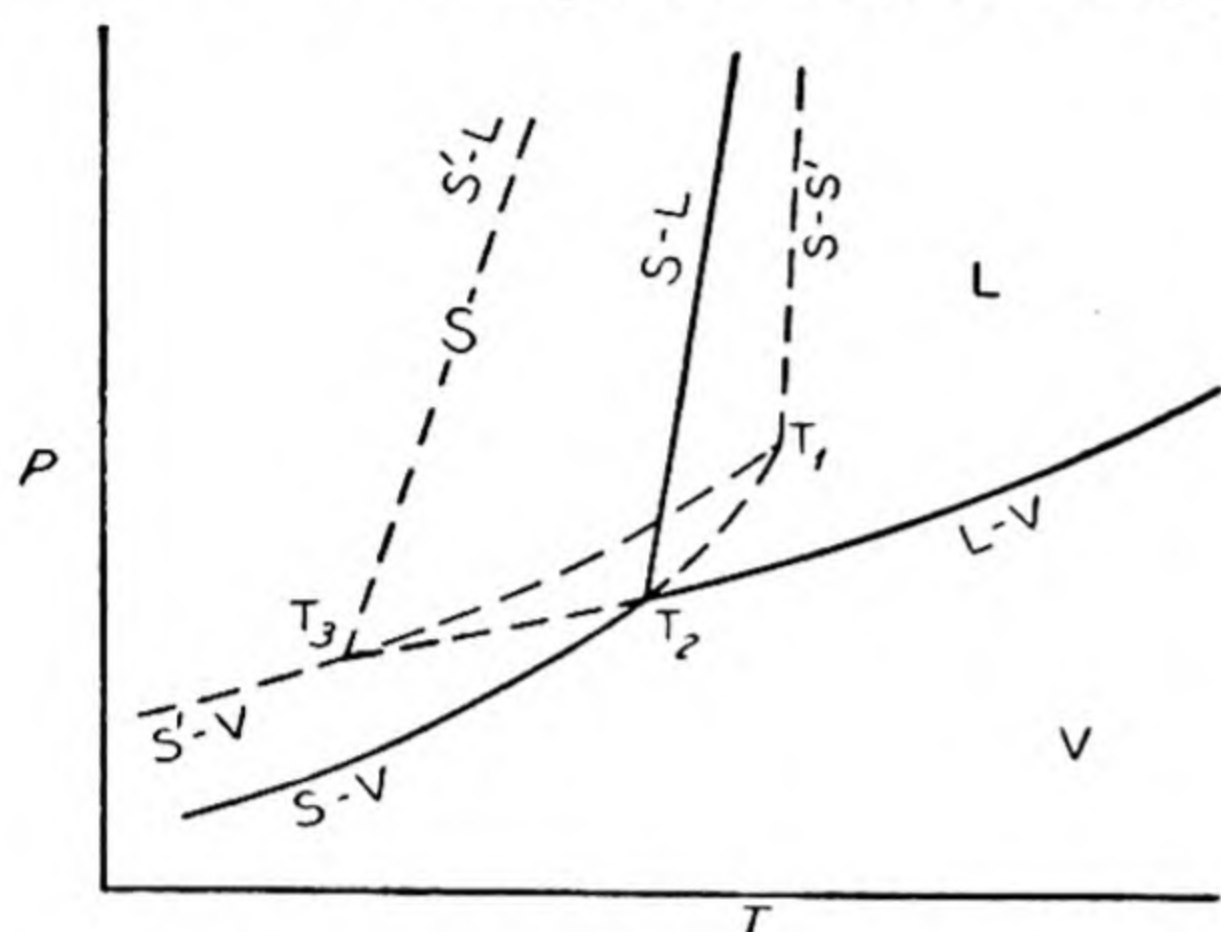


FIG. 2-15. Monotropy

point (T_1) is below the melting points (T_2, T_3) in the first case (Fig. 2-8) and above them (T_3, T_2) in the second. In Fig. 2-15, then, which is the usual picture of monotropy, T_3 is the (metastable) melting point of the monotropic form, S' , T_2 the melting point of S , and T_1 the (imaginary) transition point, $SS'V$. But these relations are seen to be identical with the suggestions shown in the lower part of Fig. 2-12, for high

pressure polymorphism, so that it is possible that the two cases may be related. The high pressure polymorph, S_h of Fig. 2-12, may conceivably appear as a monotropic form at low pressure (at the vapor pressure of the system), while the monotropic form S' of Fig. 2-15 may appear as a stable form in the condensed system under high P .

In the case of phosphorus we have not only the familiar white (or yellow) and red (or violet) forms, but also a black form obtainable from the white at $\sim 200^\circ$ under a pressure of 12,000 kg/cm².¹⁹ The stability relations of the three forms are not clear. Under ordinary pressure the white changes spontaneously to the red, which does not further transform to the black. According to heats of reaction with bromine, however, it is possible that the black crystalline variety may be the most stable of the three.²⁰ Fig. 2-16 is the usual P/T diagram for the relations of the white and red forms, or for the system under its own pressure.²¹ Besides the monotropic relation of the white to the red form we see here a case of enantiotropy of the monotropic form itself, which exists in a hexagonal form (α) below the (metastable) transition temperature of -77° (T_α), and as a regular crystal form, β , of the cubic family, between -77° and its melting point, T_β , at 44° (0.181 mm). Fig. 2-16 is schematic and neglects pseudobinary behavior. Similar polymorphism of red phosphorus has recently been suggested as part of

¹⁹ P. W. Bridgman, *J. Am. Chem. Soc.*, **36**, 1344 (1914).

²⁰ For a summary, see D. M. Yost and H. Russell, *Systematic Inorganic Chemistry*, Prentice-Hall, N. Y., 1944; pp. 157-165.

²¹ The diagram given by Smits (Ref. R-1, *Theory of Allotropy*, Longmans, London, 1922; p. 259) differs from this in showing black phosphorus as a stable high pressure form, with a stable triple point for red + black + liquid.

the explanation of the variable properties of this form.²² The stable triple point, O or T_2 , is at 590° and 43 atm, and the critical point K at $\sim 700^\circ$ and ~ 90 atm. In Fig. 2-16, 280° is the normal boiling point of white phosphorus and 420° the normal sublimation point of red phosphorus. The metastability of the white form with respect to the red is seen, of course,

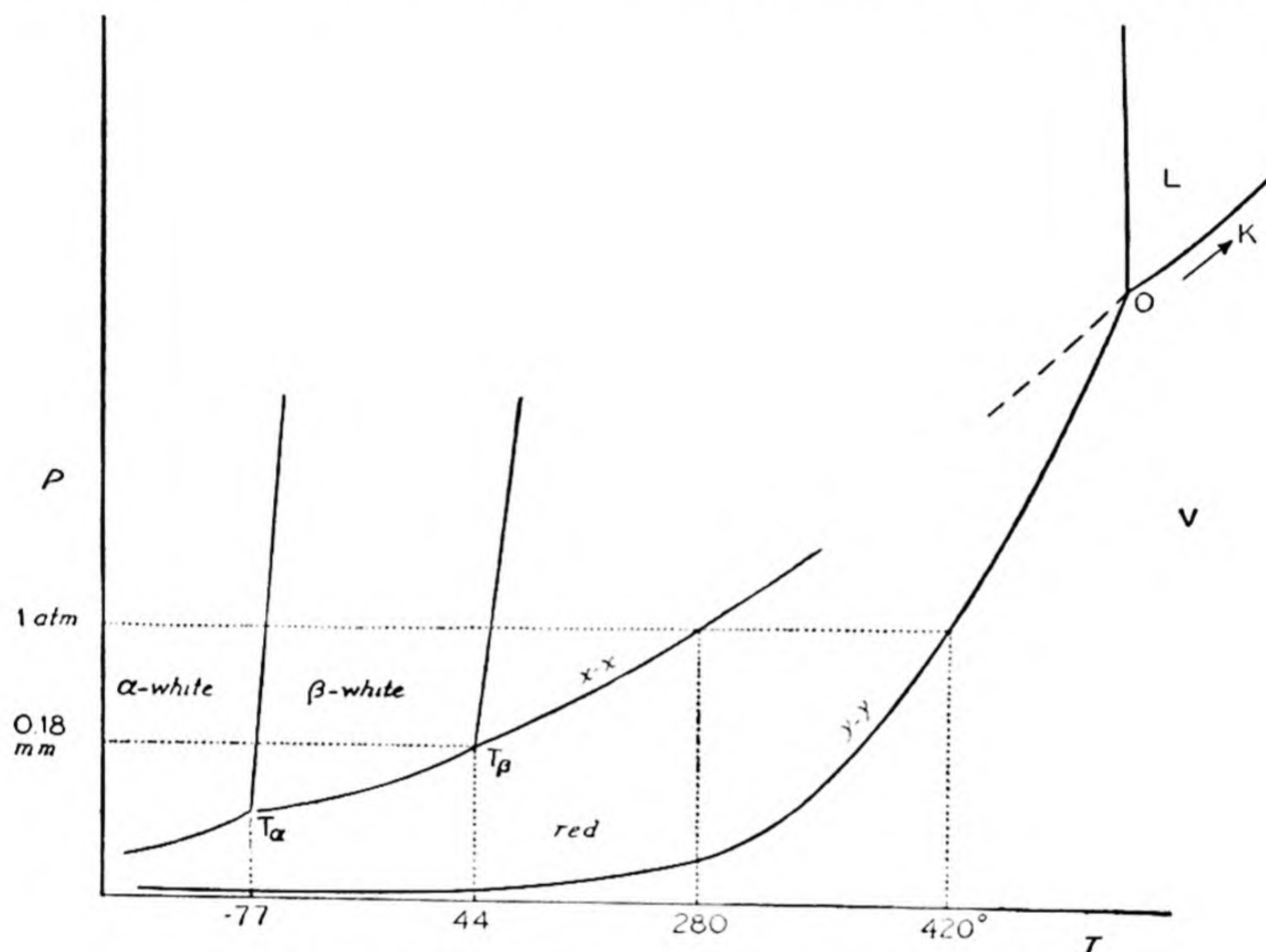


FIG. 2-16. Phosphorus diagram (schematic).

in the fact that the vapor pressure curve of the former always lies above the vapor pressure curve of the latter. Indeed, distillation from low to high temperature becomes possible (but always from the monotropic to the stable variety) since the vapor pressure of liquid white phosphorus along the region of its curve marked $x-x$, for example, is higher than the vapor pressure of solid red phosphorus at still higher temperature, $y-y$.

²² W. L. Roth, T. W. De Witt, and A. J. Smith, *J. Am. Chem. Soc.*, **69**, 2881 (1947).

Chapter III Binary Systems with Complete Miscibility in All States

A. Space Model

If two substances, A and B, are completely miscible in all three states S, L, V, we have the simplest possible phase diagram of a binary system. With only three phases possible there is no invariant equilibrium. The phase diagram is merely the extension of the P/T diagram of a one-component system, stretched smoothly and continuously from the plane of one component to the plane of the other, through the third dimension of composition. But a binary 2-phase equilibrium now involves binary phases of different composition at the same P and T ; hence each 2-phase line of one component is joined to the corresponding 2-phase line of the other by two continuous surfaces of 2-phase equilibrium, each surface representing one of the binary phases involved in the equilibrium. These surfaces are called the liquidus and vaporus surfaces for the $L \rightleftharpoons V$ transition, solidus and vaporus for $S \rightleftharpoons V$, and solidus and liquidus for $S \rightleftharpoons L$. As a result the relations of each binary 2-phase transition ($S \rightleftharpoons L$, $S \rightleftharpoons V$, $L \rightleftharpoons V$) will appear, in isothermal or isobaric section, as a *loop* made up of two continuous curves meeting at the composition of each pure component. For the $L \rightleftharpoons V$ transition the liquidus surface lies above the vaporus in respect to

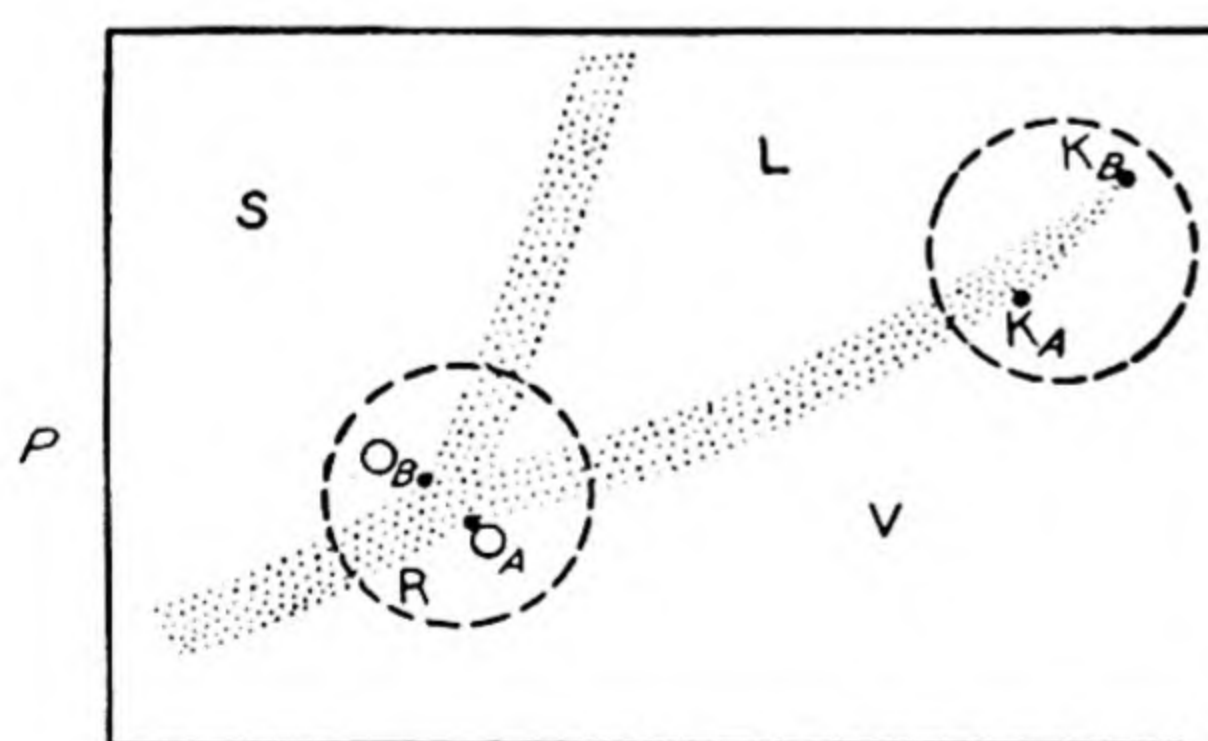


FIG. 3-1. P/T projection (T as abscissa).

P and below it in respect to T . Between these surfaces, or in the “L/V loop,” the system is a heterogeneous 2-phase mixture of $L + V$.

Schematically, in P/T projection, these general relations are shown in Fig. 3-1. Here we have, in projection, three spaces of the “space model” or 3-dimensional $P/T/c$ figure, each representing one of the binary phases S, L, V. The composition axis is normal to the paper with component A on

the paper and B above the plane. The binary LV equilibrium stretches as a hollow loop between the LV curve of A and that of B, and similar loops join the two SL and the two SV lines. Fig. 3-2 pictures the 3-dimensional

space model of which Fig. 3-1 is a projection; in Fig. 3-2 the S/V loop is shown sectioned vertically at constant T , and the S/L and L/V loops are shown sectioned horizontally at constant P . The vertical, isothermal section will be called the $(P/c)_T$ diagram, and the horizontal, isobaric section the $(T/c)_P$ diagram. In such diagrams the composition axis may represent either weight percentage or mole fraction.

The lower circled region of Fig. 3-1 will be called the melting region of the binary system, in which point O_A is joined to O_B by three continuous curves, those of the only 3-phase equilibrium (SLV) of the system. The upper circled region is the critical region, in which a critical curve runs from K_A to K_B .

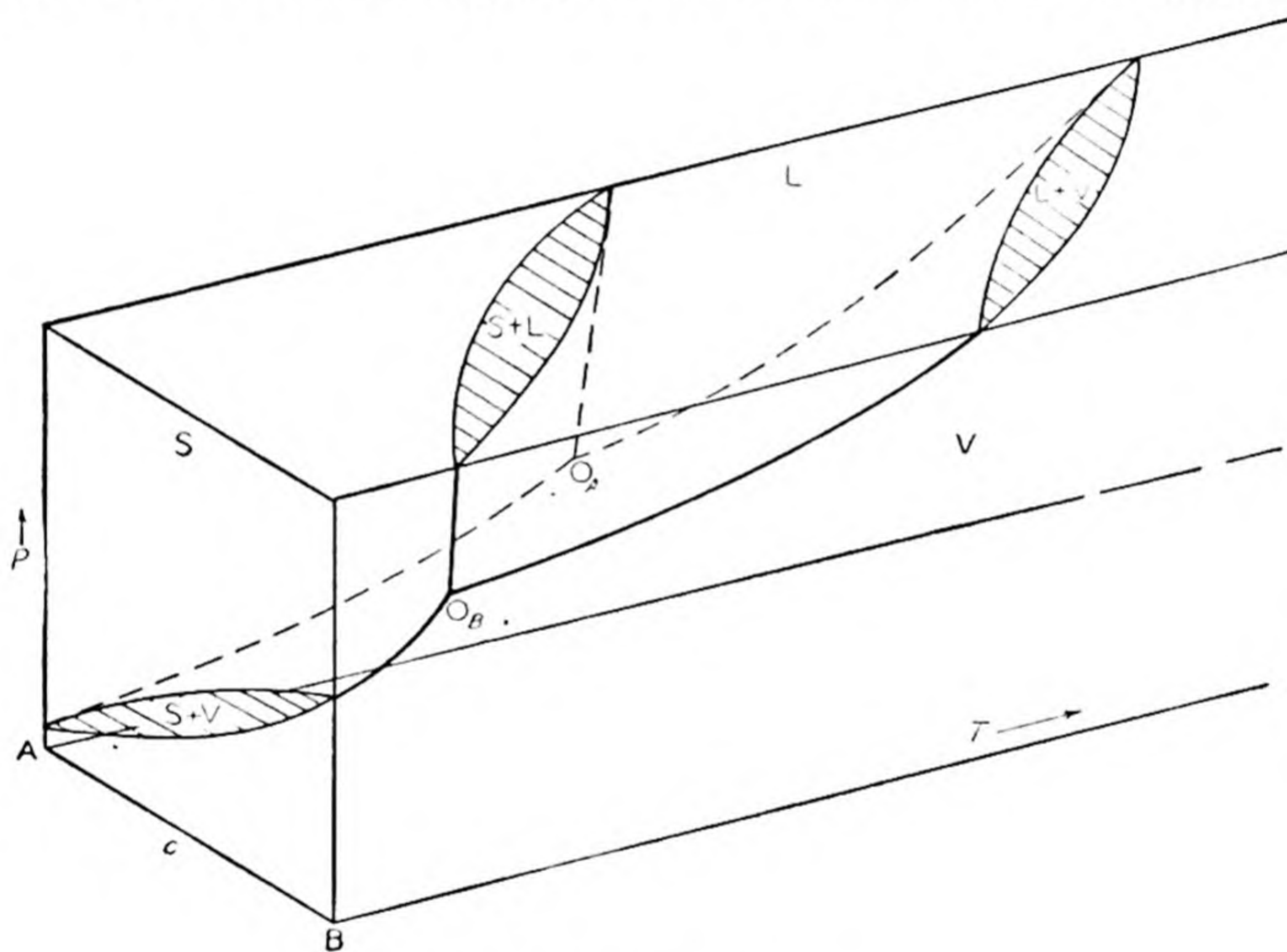


FIG. 3-2. $P/T/c$ diagram.

As stated earlier, the phase diagram does not give the properties of the system. For particular purposes, solid models representing the density or the heat content, for example, as $f(T, c)_P$ or $f(P, c)_T$, etc., may be constructed. Thus Tammann gives "the surfaces of heat content" for various types of condensed binary systems, 3-dimensional models of H , T , c at constant P , or with the pressure variable ignored.¹

B. Cross-sections of the Transition Loops

For the study of cross-sections we must assume some particular relation between O_A and O_B . The case chosen in Fig. 3-1 is that with O_B below O_A in temperature but higher in pressure, and with positive P/T slope for both SL curves. Furthermore, we shall define, as earlier, the transition *Phase*

¹ G. Tammann (Ref. S-1), *Textbook of Metallography*, pp. 164-177.

1 \rightarrow Phase 2 as that occurring with increasing T at constant P , that is, $S \rightarrow L$, $S \rightarrow V$, $L \rightarrow V$.

1. The the first type of loop is the simple or **ascendant type**, with no maximum or minimum in its $(P/c)_T$ or $(T/c)_P$ cross-section (Fig. 3-3).

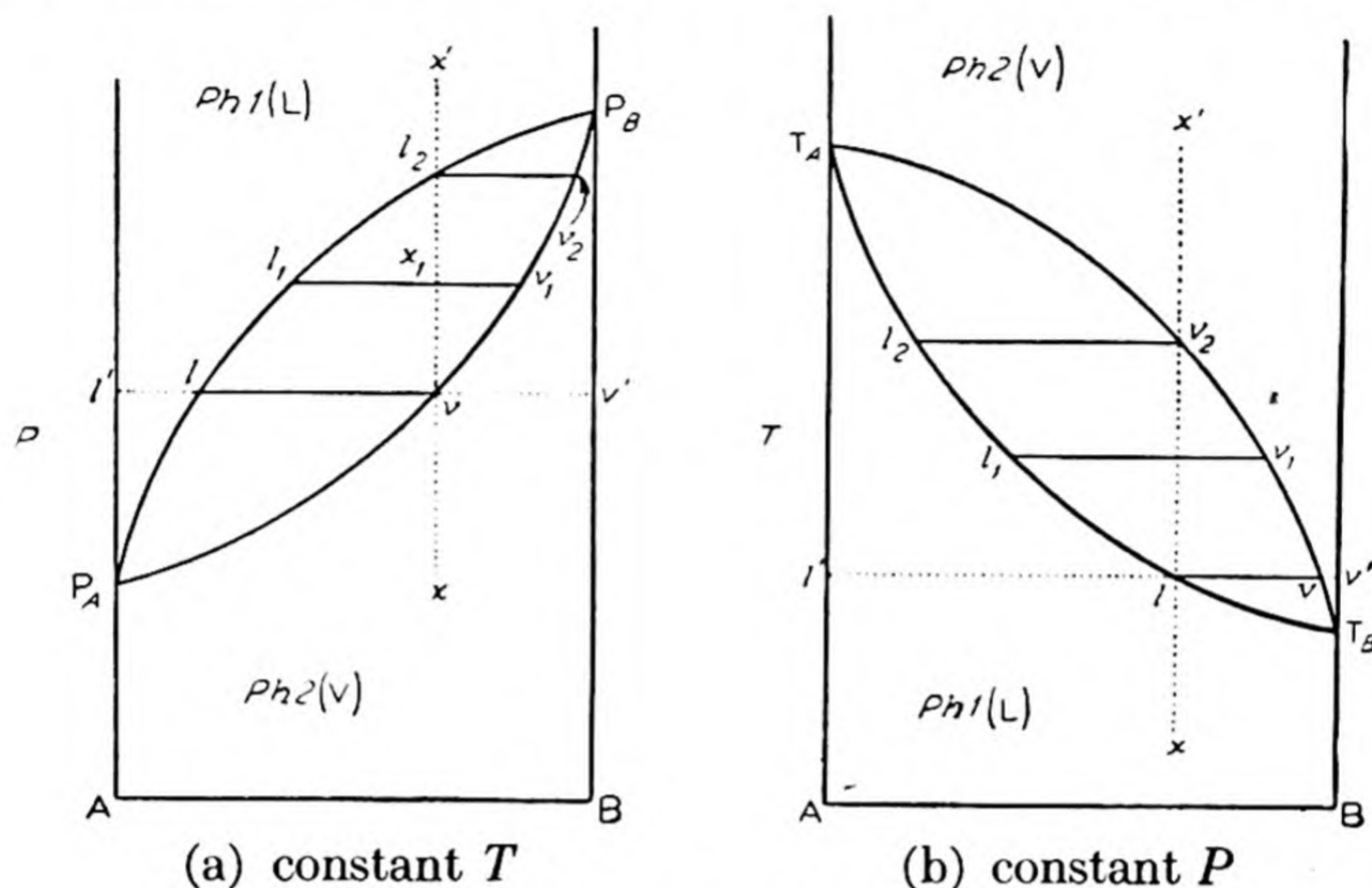


FIG. 3-3. Phase transition loops.

In Fig. 3-3(a), P_A is the transition P , at the temperature of the section, for pure A: solidification of L or V, liquefaction of V; in Fig. 3-3(b), T_A is the transition T , at the pressure of the section, for pure A: vaporization of S or L, liquefaction of S. In the following discussion, we shall consider specifically at least the $L \rightleftharpoons V$ transition since it is the most familiar, but with $Ph\ 1$ for L and $Ph\ 2$ for V the discussion is general for all three transition loops of the system. For values of P and c lying outside the loop of Fig. 3-3(a), then, the system is in one phase, a binary liquid above the liquidus (here a curve), a binary vapor below the vaporus. Within the loop, which is to be imagined as filled with isothermal, isobaric tie-lines, the system exists in two phases, the compositions of the coexisting phases being given by the ends of the tie-lines.

A vapor of composition x in Fig. 3-3(a), subjected to increasing P (at constant T), forms at P_v an infinitesimal amount of liquid of composition l ; P_v may be called the "dew point" pressure of the vapor x at this temperature. As P rises further, the two phases change in composition along the equilibrium curves, so that at P_{v1} the phases have the compositions v_1 and l_1 and the ratio of the amount (mass or moles) of the vapor phase to that of the liquid is l_1x_1/x_1v_1 .² At P_{v2} the sample is completely liquefied, the last

² For graphical representation of binary, ternary and quaternary systems, intended to show changes in the relative amounts of phases during change in temperature, see R. Bertschinger, *Z. Metallkunde*, 30, 360 (1938).

vapor disappearing being an infinitesimal amount with the composition v_2 . In reverse, the liquid, again of composition $x' (= x)$, first produces a gas when the pressure is lowered to the liquidus, P_{l_2} ; hence this curve may be called the "bubble point curve" for the specified temperature. In Fig. 3-3(b) a liquid x first produces vapor, of composition v , when the temperature reaches the liquidus, which may now still be called a bubble point curve, but better the boiling point curve at the pressure of the diagram. The composition and relative amounts of l and v are again given by the tie-lines in the loop, until at T_{c_2} the liquid (l_2) finally disappears leaving a vapor v_2 as sole phase. In reverse the vapor x' first condenses some liquid when cooled to the vaporus, which is therefore the condensation or dew point curve for the specified pressure.

If the system is "ideal" in both phases these curves may be calculated or constructed. This is possible, for example, from the LV curves of the separate components, by familiar methods, or in general, from the separate *Ph 1-Ph 2* curves of the components, as in the ideal equations for the SL curves at constant P derived by Seltz.³ The ideal $(P/c)_T$ diagram, for example, for the equilibria LV and SV, has a straight line for the *Ph 1* phase, that is, L in LV, because the total P is a linear function of the composition of the liquid; with ideal systems these two curves draw farther apart (or the vaporus becomes more bowed in 3(a)), the farther apart are the individual transition pressures or temperatures. This effect bears on the question of solubility. In Fig. 3-3(a) the distance $l'l$ is the solubility of the gas B in liquid A, at the specified T and P ; and $v'v$ is the solubility of the liquid A in the gas B at the same T and P . Similarly, if *Ph 1* and *Ph 2* refer respectively to solid and liquid, then in Fig. 3-3(b), $v'v$ is the solubility of solid A in liquid B, and $l'l$ the solubility of liquid B in solid A, at the same T and P . With only two phases involved, the solubility depends on both P and T . Fig. 3-3 shows, furthermore, that for specified P and T the solubility of the gas B in liquid or solid A increases with the condensability, that is, as T_B rises) or decreases with increasing volatility (or as P_B rises) of the gas. Similarly, the solubility of solid A in liquid B, at specified T and P , increases with the fusibility of the solid, that is, as T_A of Fig. 3-3(b) decreases.

The transformations already discussed in connection with Fig. 3-3 refer to operations in closed systems, at constant P or T , but not at constant volume. If the liquid x of Fig. 3-3(b), however, is heated at constant volume, both its P and T rise, but it never vaporizes or boils, since the volume of the vapor is greater than that of the liquid. If, on the other hand, the vapor x' , also of composition x , but above the vaporus, is cooled at

³ H. Seltz, *J. Am. Chem. Soc.*, **56**, 307 (1934). For consideration of conditions of non-ideality, see H. Seltz, *ibid.*, **57**, 391 (1935), and G. Scatchard, *ibid.*, **62**, 2126 (1940).

constant volume, it may or may not undergo the particular phase transition, depending upon the total volume and upon the specific volumes of the possible phases as function of T , P , and c . This kind of change may not be generalized, therefore, without hypothetical assumptions about these phase properties; but some discussion of the possibilities is found in Roozeboom^{4a} and in Vogel's book.^{4b}

Boiling in the open air varies from the process already discussed for Fig. 3-3(b) in that the vapor is presumably removed as rapidly as it is formed. If the figure represents atmospheric pressure, it gives the normal boiling point curve of the binary system. If we neglect the loss of vapor in reaching T_l , the mixture x begins to boil (in air) at T_l . As vapor is removed during boiling, the residual liquid becomes richer in A and rises in boiling point, along the curve ll_1T_A ; and it is possible then, in this "ascendant" type of system, to approach a residue which is pure A. As T_A is approached, the vapor being lost also approaches pure A, so that A is reached only as a possible limit. In the case of the $L \rightarrow S$ freezing equilibrium, this process corresponds to the skimming off of the solid phase, if possible, as it is produced, so that the residual liquid approaches the composition B as its freezing point falls. In each case the purest sample of the separating component (B in vapor, A in solid) is that which is first produced on boiling or on freezing. In a closed system at constant P the liquid x boils over the range $T_l - T_{v_2}$; with removal of vapor, the range may extend to T_A . Similarly if x' is a binary liquid forming continuous solid solution, it has a freezing point range from T_{v_2} to T_l , whereas if the solid is continually removed (or, with the same effect, if the solid first formed does not undergo change in composition along the curve l_2l , as a result of too rapid cooling) then the range may extend to T_B .⁵

Distillation is a special process applied to the $L \rightleftharpoons V$ transition, in which, at constant P , a binary liquid is heated at one point (the boiler of the system) and the vapor produced is liquefied by cooling at another point (the condenser). If there are no regions of intermediate temperatures, then it is a simple open air boiling process with recovery of the liquefied vapor, which may be collected in fractions, according either to volume or to temperature ranges of the boiler, the boiling point still being given by Fig. 3-3(b), from T_l as the initial to T_A as the final boiling point. From the flat-

^{4a} H. W. Bakhuis Roozeboom (Ref. P), *Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*, Braunschweig, 1901; Vol. II, part 1, p. 146.

^{4b} R. Vogel (Ref. V), *Die Heterogenen Gleichgewichte*, Leipzig, 1937; p. 137.

⁵ The relation between phase compositions and temperature during the course of such transition in the boiling of a binary liquid or in the solidification of a binary melt has been discussed by A. E. Korvezee and F. E. C. Scheffer, *Rec. trav. chim. Pays-Bas*, **60**, 732 (1941); these authors call the process a transition "without rectification."

ness of the liquidus near T_B in Fig. 3-3(b), it is seen that most of the volatile component B will boil over through a small range of temperature, and that near the end of the process the composition of the residue hardly changes through a considerable rise of boiling point. Since each fraction may be subjected separately to the same treatment, various sequences are possible, for "fractional distillation," in which the residue of the first (most volatile) fraction is added to the second before distillation of the latter, etc. (Similar fractionation procedures apply to separation of A and B through crystallization.) On the other hand, if many stages, at intermediate temperatures, for the attainment of liquid-vapor equilibrium, are interposed between the boiler and the condenser (refluxing, rectification), a continuous process of separation by distillation becomes possible.

For the efficiency of fractionation, we may define $(x_A)_1/(x_A)_2$, the ratio of the mole fraction of A in *Ph 1* to its mole fraction in *Ph 2*, as the factor for the retention of A in *Ph 1*, such as the retention of A, the less volatile component, in the liquid during evaporation. In the ideal case the efficiency then depends on the ratio of the transition pressures of the separate components; it may be shown that $(x_A)_1/(x_A)_2$, at constant T , $= (x_A)_1 + (x_B)_1 P_B/P_A$. Since $d \ln(P_B/P_A)/dT = (\Delta H_B - \Delta H_A)/RT^2$, it follows that the separation is more efficient in distillation at lower T and therefore at reduced pressures.⁶

In contrast to these processes, a binary liquid may be evaporated at constant T in the open. Now the total gas pressure is constant (atmospheric), but the vapor pressure of the binary liquid will vary as its composition changes by removal of the vapor. The liquid evaporates, without boiling, provided that the partial pressures of its components in the equilibrium vapor, for the specified T , are smaller than their prevailing partial pressures in the atmosphere. In this case, Fig. 3-3(a) applies; the liquid evaporates, at constant T , becoming richer in A, while its vapor pressure falls toward that of pure A.

2. The 2-phase transition curves or loops may also show a **maximum** or a **minimum** of P or T . Marked "positive" deviation from ideality, or repulsive tendency, in the *Ph 1* phase (S or L) leads to a maximum in the $(P/c)_T$ curve and a minimum in the $(T/c)_P$ loop; Fig. 3-4(a, b). Marked "negative" deviation, or attraction, in the *Ph 1* phase leads to a minimum in the $(P/c)_T$ and a maximum in the $(T/c)_P$ loop, Fig. 3-4(c, d).

Before discussing these equilibria further, we note, for future use, that, as long as the transition curves involved have *positive* P/T slopes, the T/c section is of the same form as the P/c , turned upside down, in respect to rela-

⁶ J. H. Hildebrand, *Solubility of Non-Electrolytes*, Reinhold, N. Y., 1936; p. 29.

tion of curves, identity of phases, etc., for those parts of the system not involving the "melting region." This will hold true even later, for more complex cases, including even the diagrams of ternary systems.

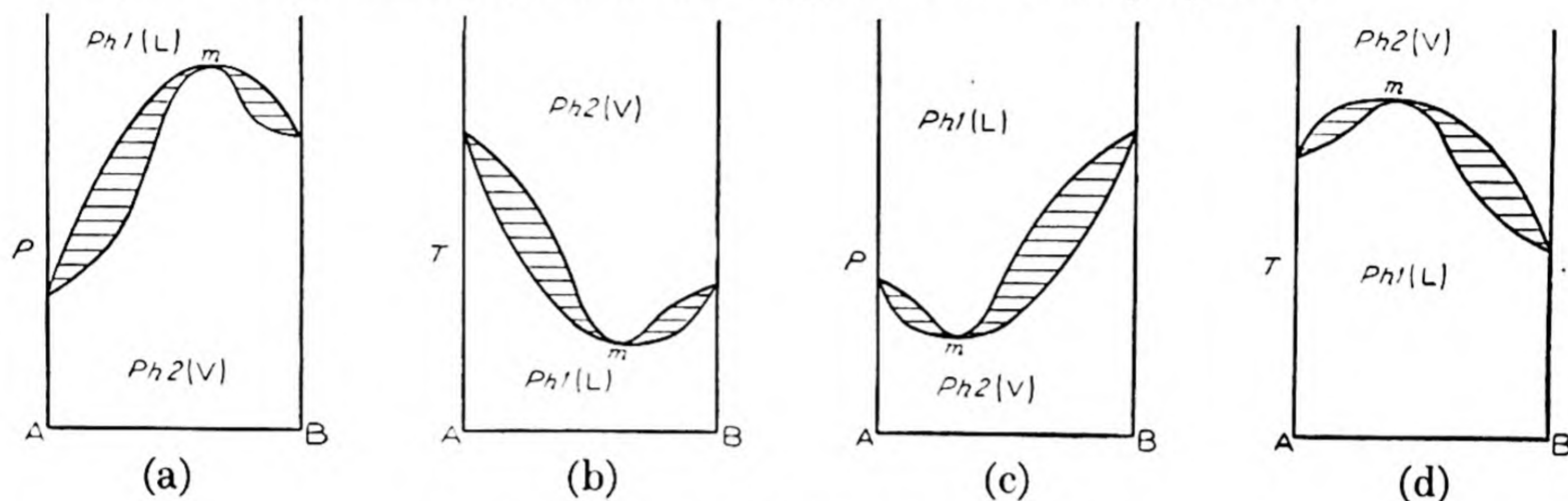


FIG. 3-4. Azeotropic phase transitions.

The parts of Fig. 3-4 on either side of a maximum or a minimum (point m) may be treated independently just as the curves of Fig. 3-3. If liquids on either side of m , of Fig. 3-4(d), are boiled, they change in composition as their boiling point rises, giving in either case the liquid of maximum boiling point, or the "constant boiling solution," of composition m , which then boils at constant T , to a vapor of the same composition. On either side, the relative position of the two curves, vaporus and liquidus, is given by Konowalov's rule⁷ (which may be derived from the Duhem-Margulies equation) that the vapor is always richer in that component which causes a rise in the vapor pressure of the liquid or a fall in its boiling point. The rule is seen to apply to all the curves of Figs. 3-3 and 3-4, and may obviously be generalized to any of the $Ph\ 1 \rightleftharpoons Ph\ 2$ transitions. The two continuous curves of such a 2-phase transition touch only at a maximum or a minimum of T or P , except of course at the sides of the diagram,⁸ or, in other words, only at points where the transition T or transition P becomes constant because the two phases have the same composition. Contact at any other point, as will be discussed later (Chapter VII), would indicate the existence of a compound of such stability as to divide the system into two independent binary systems.

The two curves (L and V) are continuous and smooth through m ; their angle of contact is tangential and not the same as at the sides of the diagram. In either case, however, the tie-lines vanish to points and cannot be used to give the relative amounts of the coexisting phases. In a binary system, tie-lines of the phase diagram may be used for the proportions of the phases only in a 2-phase equilibrium, and then only if the phases differ in composition.

⁷ D. Konowalov, *Ann. Physik*, **14**, 219 (1881).

⁸ See Gibbs (Ref. H), Vol. I, p. 99.

Finally, the composition of the system at m is not constant but varies with P and T , describing, in the 3-dimensional space model of the binary system, a line, $c_m = f(P, T)$, of "restricted univariance," as discussed in Chapter I. With change in P or T , it is also possible for the maximum or the minimum to disappear, especially with rising T , so that the system may become of the simple or ascendant type, in its liquid-vapor relations, before the critical region is reached.

In systems of the type of Fig. 3-4, fractionation by means of the 2-phase transition involved cannot be carried through the point m , at constant P or at constant T . When a maximum or minimum occurs in the L/V loop, the system is known as **azeotropic**,⁹ since it is possible for a liquid of particular composition, c_m , to boil, at constant P , without change in composition during the course of transition, to a vapor of the same composition. If the system is azeotropic with minimum boiling point, as in Fig. 3-4(b), the boiling point of liquids on either side of m rises during boiling or distillation toward the pure components. With $c < c_m$ (in respect to B) it is possible to approach pure A as a final liquid residue, but it is not possible to obtain a greater concentration than c_m in respect to B, for the condensate. If the system is azeotropic with a maximum boiling point, as in Fig. 3-4(d), pure components may be approached as condensates on either side of m (B for $c > c_m$; A for $c < c_m$), but the liquid residue, on continued boiling, is c_m , the "constant boiling" solution. The separation by distillation may however become possible, either by boiling at different pressures, causing a shift or disappearance of the maximum or minimum, or by boiling in the presence of some third component, the effect of which for the present may be said to be similar to that of a variation in P .

The following may be mentioned as examples of the curves of Figs. 3-3 and 4-4: for liquid-vapor relations the system water-acetone is ascendant, the systems acetone-chloroform and $\text{H}_2\text{O}-\text{SO}_3$ have P -minima and hence T -maxima, and the systems alcohol-water and alcohol-chloroform¹⁰ have P -maxima and hence T -minima; for solid-liquid relations the system Au-Ag is ascendant, the system *d*-carvoxime-*l*-carvoxime has a T -maximum and the system $\text{Na}_2\text{CO}_3-\text{K}_2\text{CO}_3$ has a T -minimum.

C. The Critical Region ($L = V$)

The chief difference, in respect to the phase diagram, between the liquid-vapor and the other two bivariant equilibria, is that the L/V loop ends at a

⁹ J. Wade and R. W. Merriman, *J. Chem. Soc.*, **101**, 997 (1911); the simple or ascendant type may accordingly be called "zeotropic," a term used by Bowden (Ref. D), *The Phase Rule and Phase Reactions*, Macmillan, London, 1938.

¹⁰ G. Scatchard and C. L. Raymond, *J. Am. Chem. Soc.*, **60**, 1278 (1938).

critical curve, connecting the critical points of the components. In the very simple system we are now considering (single solid solution and single liquid phase) the L/V loop may be expected to continue, without interruption, to the binary critical curve, so that only "unsaturated" systems, that is, systems not in equilibrium with any solid, show the critical phenomenon. With K_A below K_B both in P and in T , as in Fig. 3-1, the end of the L/V loop, in 3-dimensional view, is given in Fig. 3-5. The distinction between L and V phases disappears along the K- or critical curve, $K_A K_B$, so that the isothermal and isobaric sections appear as in Fig. 3-6.

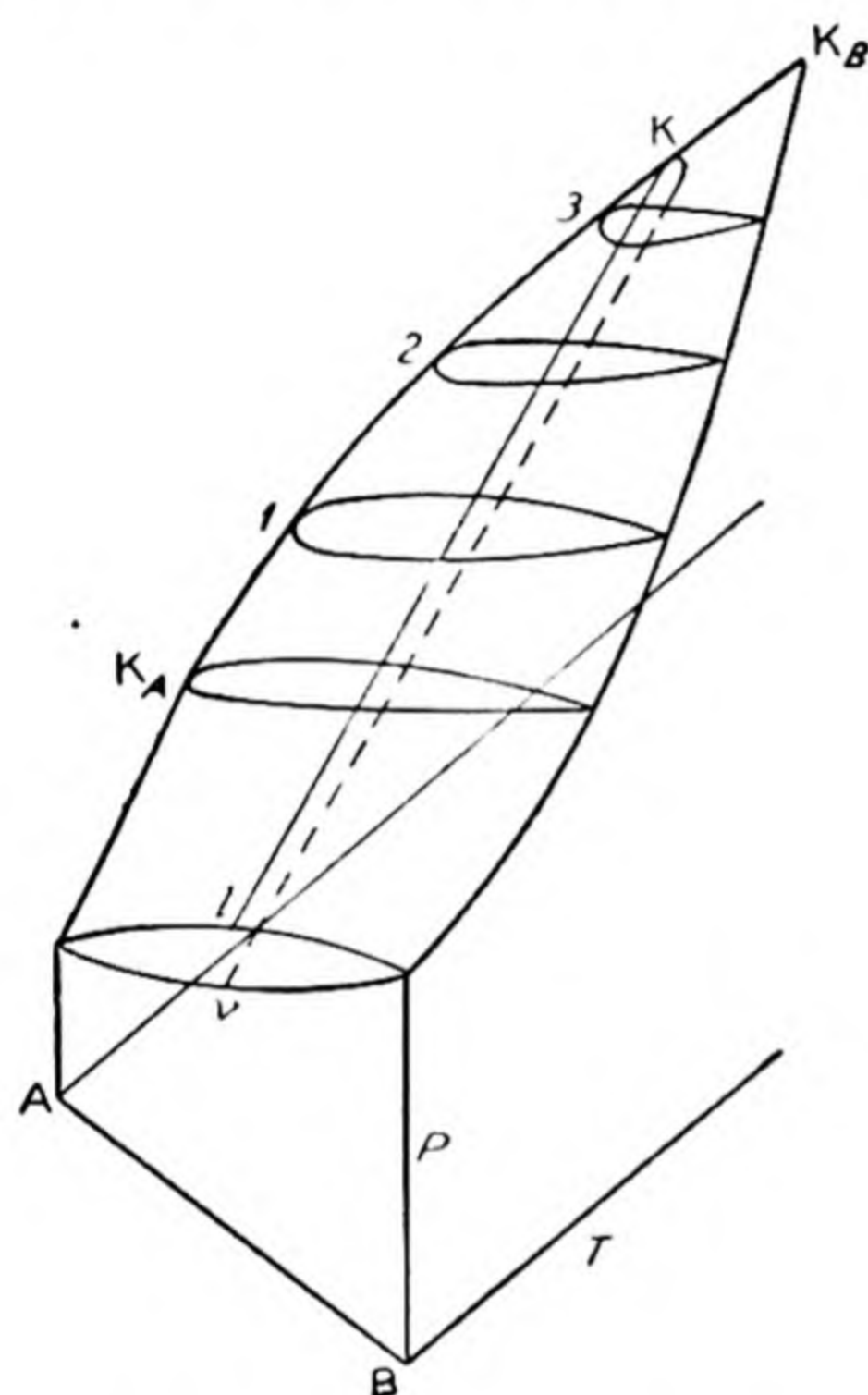


FIG. 3-5. Critical region.

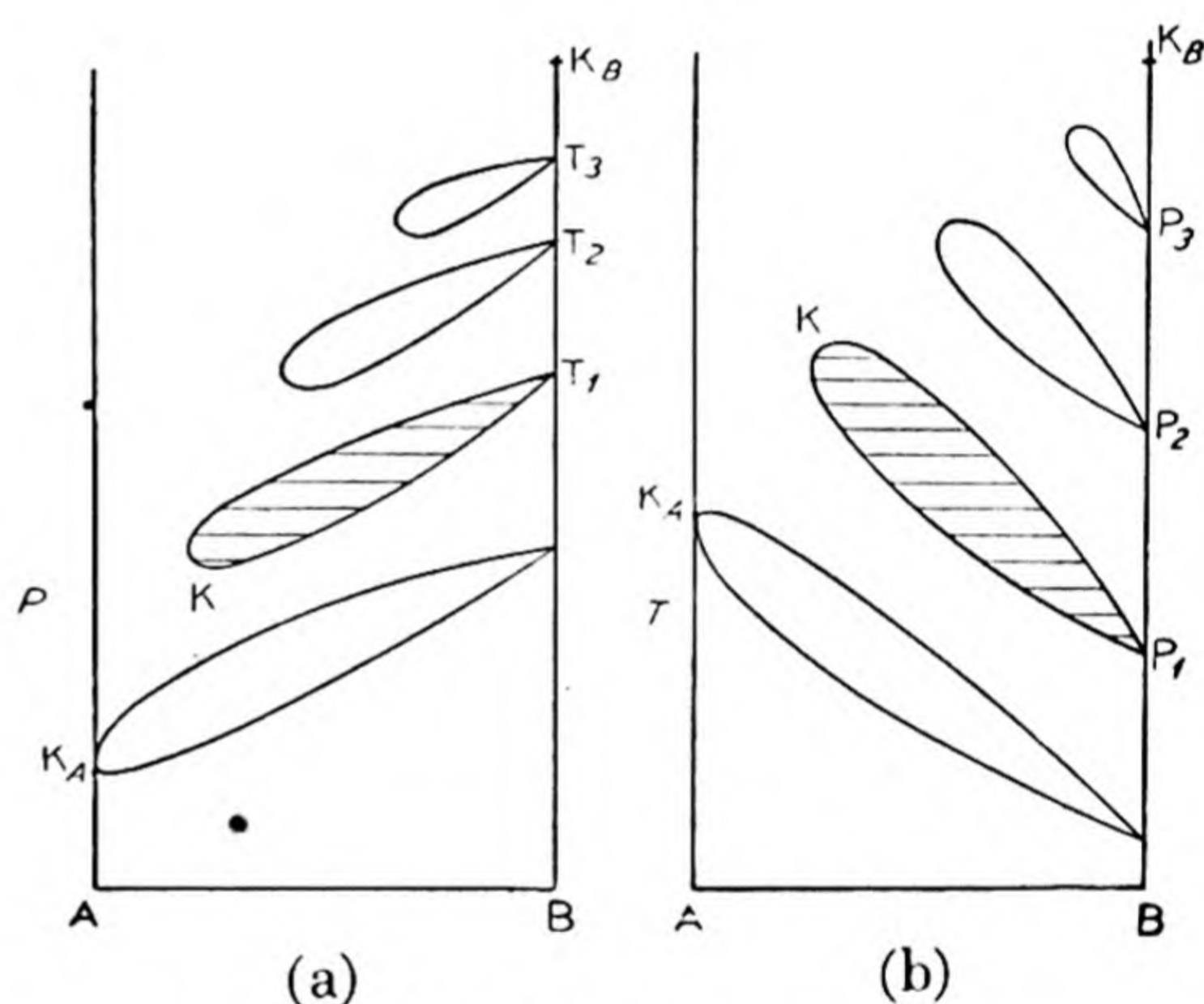


FIG. 3-6. Sections of Fig. 3-5.

Fig. 3-7 (schematic) shows a section at constant c (that is, an isopleth, or isoplethal section) in relation to the critical region. If the locus, in P , T , for a sample of the composition of the section, is above the curve lK , it is entirely liquid; below vK , entirely vapor. Within the L/V loop, shown in section as the curve lKv , it consists of L and V phases of different compositions (neither one on the plane of the Figure), their compositions and proportions being given at any point by the tie-line for that value of P and T , in Fig. 3-6. The liquidus surface, sectioned as the curve lK , is continuous with the vaporus surface, vK , around a rolling surface generated by such lKv sections between K_A and K_B , the section degenerating, of course, to a line at each end, the LV curve of each component. The critical phenomenon is observed, for each particular composition, such as that of Fig. 3-7, at special values of P and T , those of the point K , on the critical curve $K_A K_B$. This point is not necessarily the maximum of P or of T (P_m , T_m) for the

particular lKv section. The critical curve may lie between or on either side of the curves of maximum P and maximum T . In addition, the critical curve may follow various courses between K_A and K_B . Fig. 3-5 shows schematically the very simplest case, in which it rises continuously both in P and in T , from K_A to K_B , but it may also show various combinations of maxima and minima of P or T or both.¹¹

For any given composition (Fig. 3-7) cooled at constant volume from T above the critical curve, the critical phenomenon will be observed (identity of L and V , or appearance of a median meniscus giving equal volumes of identical phases) only if the density of the system corresponds to the unique relation of P , T , and c for point K . If the density is too high, the loop may be entered on the liquidus, lK , giving a discrete or non-critical phase transition, merely vaporization ("bubble point" phenomenon),

the new (vapor) phase being immediately richer in B than the original (now liquid) phase. If the density is too low, the loop may be entered through the vaporus, vK , the "dew point" or condensation surface.¹² The complex now forms, as a second phase, a liquid immediately richer in A .

At the pressure wx , between P_m and K , the sample is seen to be a single, homogeneous liquid while its position is outside the loop, and a heterogeneous system of $L + V$ if its temperature is such as to bring it within the loop. The process $L \rightleftharpoons (L + V) \rightleftharpoons L$, brought about near the critical curve by isobaric change in T or by isothermal change in P , is known as **retrograde vaporization**. The quantity of the second phase, V , first increases and then decreases, as T passes through the loop. On the other hand, if the pressure is changed along the isotherm yz , the sample undergoes **retrograde condensation**, or the change $V \rightleftharpoons (L + V) \rightleftharpoons V$, since it is now a vapor outside the loop and a heterogeneous system within the loop. If K is on one side of both P_m and T_m , only one of these retrograde processes is possible; with K on the left of P_m , and on the curve lP_m , as in Fig. 3-8, only retrograde condensation is possible. The third arrangement involves

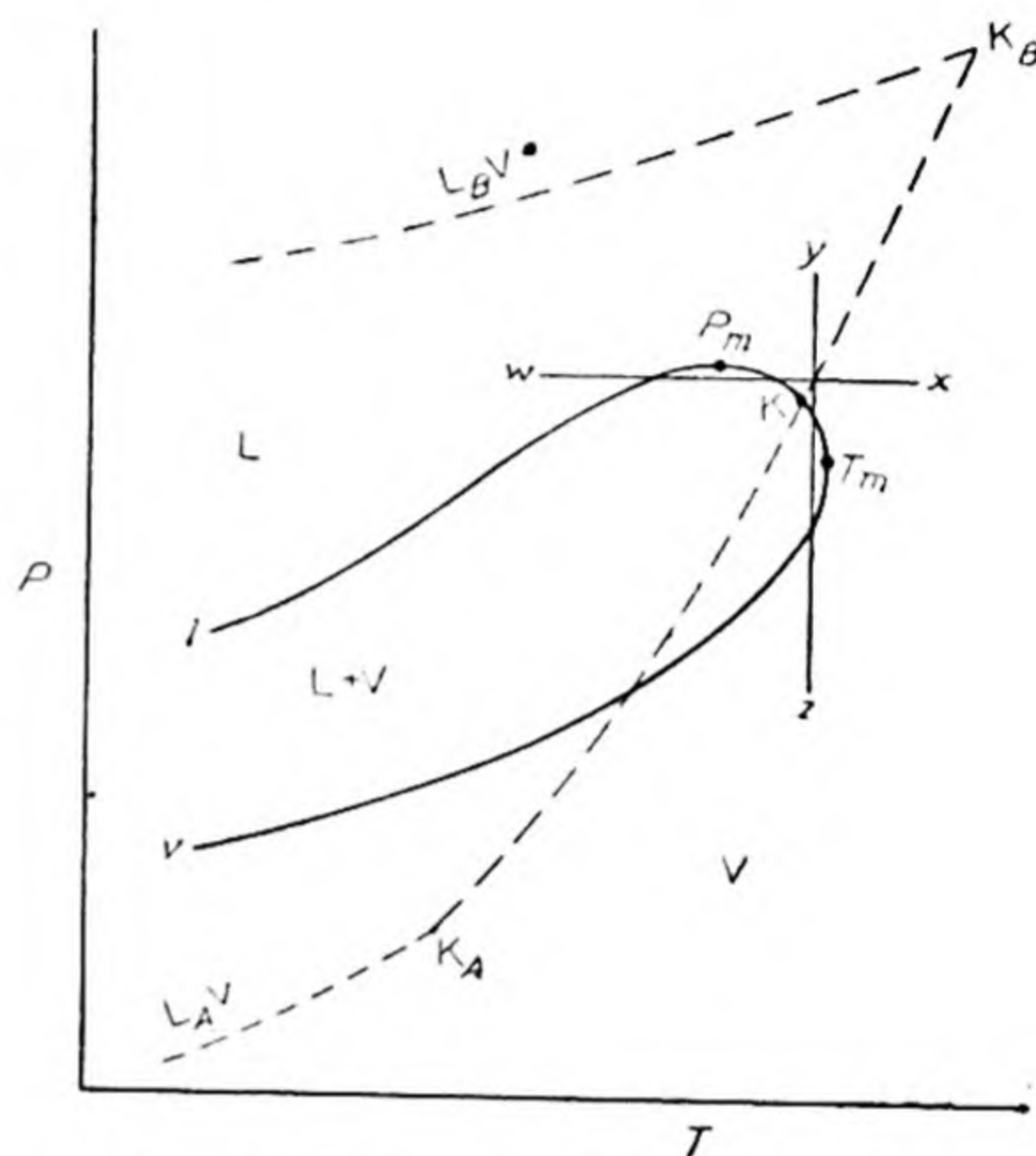


FIG. 3-7. Isopleth of Fig. 3-5.

¹¹ For examples of the various shapes of binary critical curves, see *I. C. T.*, vol. III pp. 381-2.

¹² P. Duhem, *J. Phys. Chem.*, **1**, 273 (1897), called the curves lK and vK of such a section the boiling- and dew-lines, respectively.

K on the left of T_m , on the curve vT_m . All three arrangements may be realized in a single system, depending on the composition of the section; as pointed out by Duhem,¹² this is the case for the system ethane-nitrous oxide, in which the critical curve is ascendant in respect to P but passes through a T -minimum.¹³

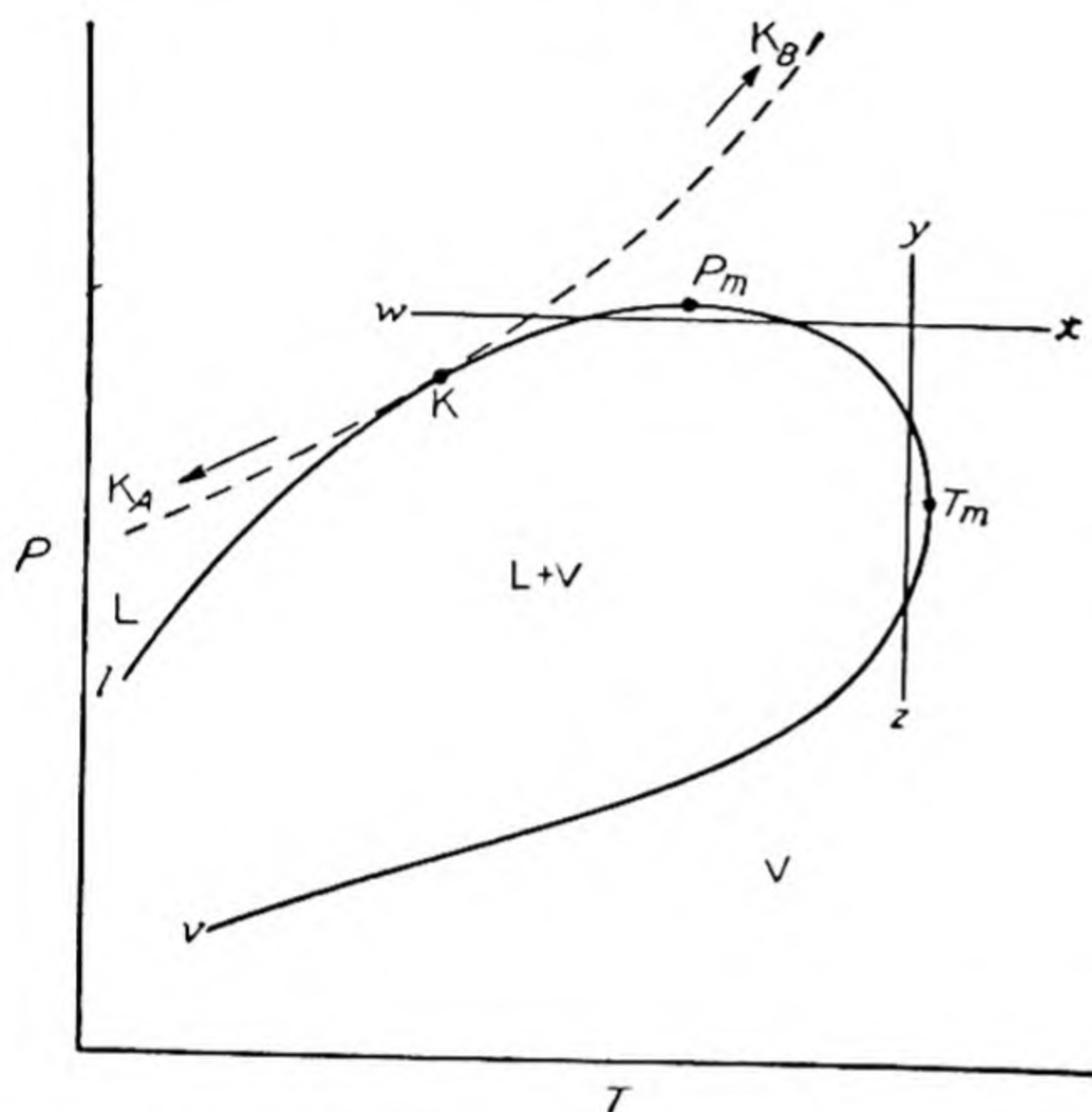


FIG. 3-8. Variation of Fig. 3-7.

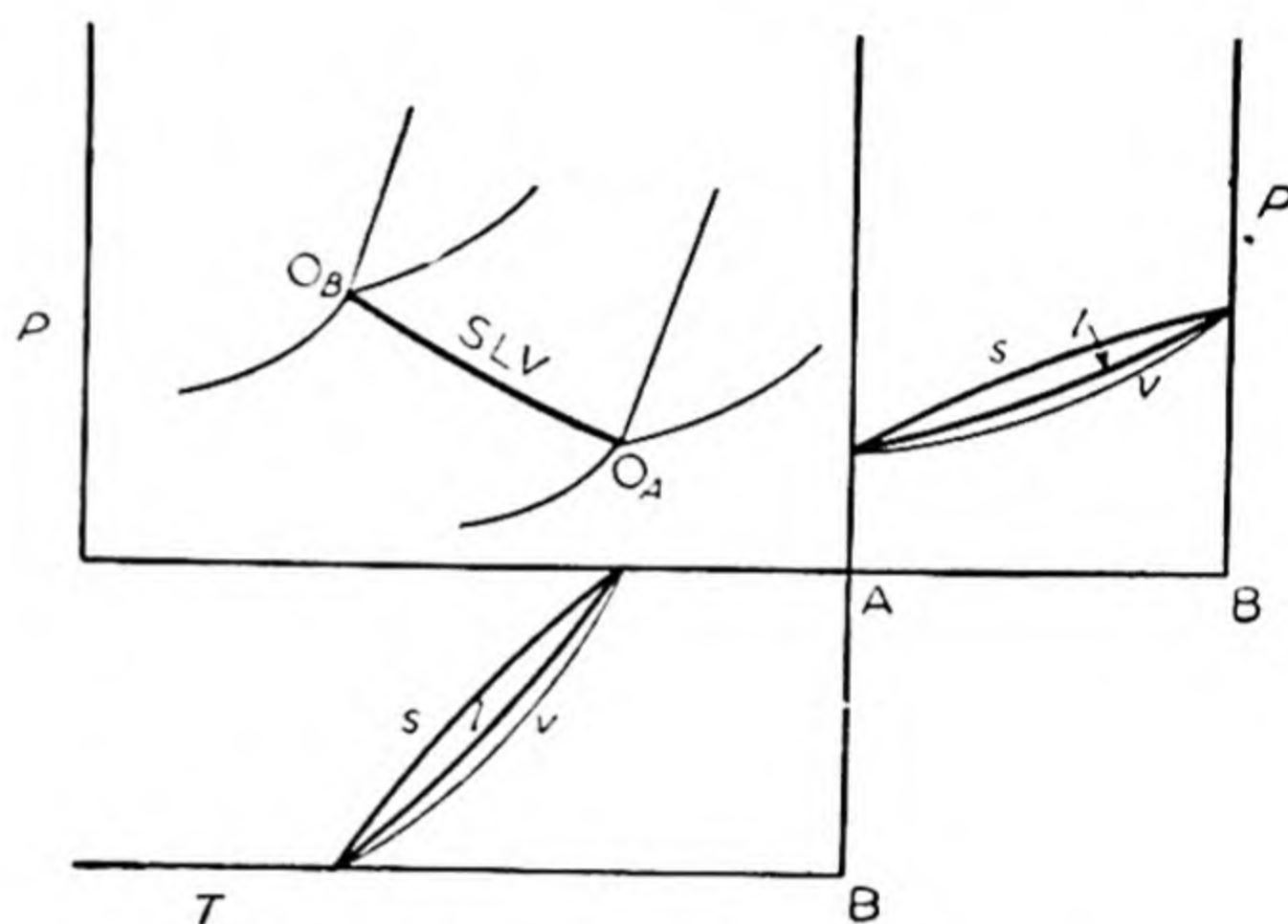


FIG. 3-9. Melting region.

D. The Melting Region, or the 3-Phase Equilibrium SLV

The 3-phase equilibrium SLV for component A, or point O_A , is extended, as the three 2-phase loops intersect each other in the melting region, as a continuous, univariant, 3-phase "melting point curve" to the triple point of B, O_B . At any value of P and T , the three binary phases in this equilibrium have various compositions, and there are therefore three curves, one for each phase, joining O_A and O_B . The univariant, 3-phase tie-lines (isothermal and isobaric), originating as points at each of these separate triple points, then generate a ruled surface which must appear as a curved line on the P/T projection.

1. If the three loops (S/L, S/V, L/V) are all of the ascendant type when they intersect, the 3-phase melting point curve will also be of the ascendant type in all its projections (P/T , P/c , T/c) (see Fig. 3-9). For the intersection of the loops we merely note that, as in the one-component diagram of Chapter II, the three 2-phase systems or loops will be cut in the usual order by isothermal or isobaric sections of the space model, depending on whether we are above or below the 3-phase or melting region, indicated as a range R of P or T . For the original relation assumed between O_A and

¹³ J. P. Kuenen, *Z. phys. Chem.*, **24**, 667 (1897).

O_B (Fig. 3-1) the isothermal sections become those of Fig. 3-10. Below T_R , the loops are cut, with increasing P , in the order S/L (m , or metastable), S/V, L/V (m); the only stable phases are S, above the S/V loop, which like all the loops must be imagined filled with tie-lines, and V below it. As T rises towards O_B , the pressures of all these equilibria rise; but relative to each other, they draw together, since their extremities are to coincide, first at O_B for pure B, and at still higher T , at O_A for pure A. The arrows in the diagrams, therefore, indicate from left to right the relative motion of these equilibria as T rises.

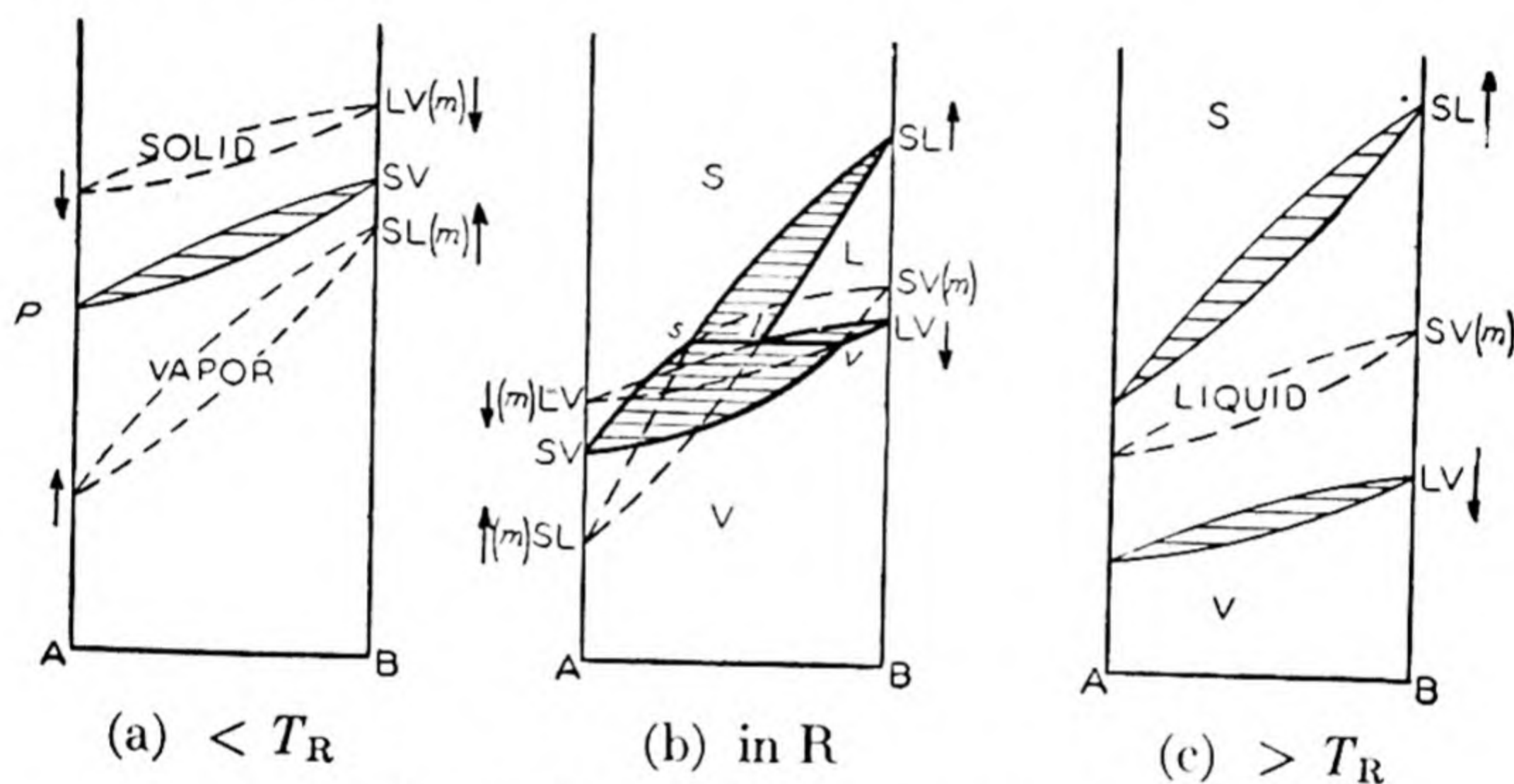


FIG. 3-10. Isotherms of Fig. 3-9.

In Fig. 3-10(b), therefore, between O_B and O_A , the successive phases for pure B, with rising P , will be V, L, S, but the order of the loops is different on the A side of the figure. As the loops interpenetrate, the nature of the stable phases for each composition is given for the isotherms by these simple principles: (1) that vapor system (between LV and SV) is stable which has the lower P ; and (2) the SL system is stable only when its P is higher than both SV and LV. Later, in the consideration of isobars, we note: (1) that vapor system is stable which has the higher temperature, and (2) the SL system is stable only when its T is lower than both the others. The process of interpenetration of the three loops shown in Fig. 3-10(b) continues, with rising T , until at O_A the three equilibria just touch for pure A, above which we have Fig. 3-10(c). In the process the 3-phase tie-line, slv , moving from O_B to O_A , describes the curves projected in Fig. 3-9. For the isobars (Fig. 3-11) the relations are analogous to those in Fig. 3-10; the 3-phase tie-line, slv , of Figs. 3-10(b) and 3-11(b) is, of course, one and the same line, at the same P and T .

The representation of the melting point region may be completed by a constant composition section, the isopleth shown in Fig. 3-12. This section shows the three 2-phase regions, S + V, S + L, L + V, the last being part

of the lKv loop of Figs. 3-5 and 3-7. The boundaries of these areas of Fig. 3-12 are sections of phase transition surfaces. As in Fig. 3-7, any system with values of P and T falling within one of these 2-phase regions consists

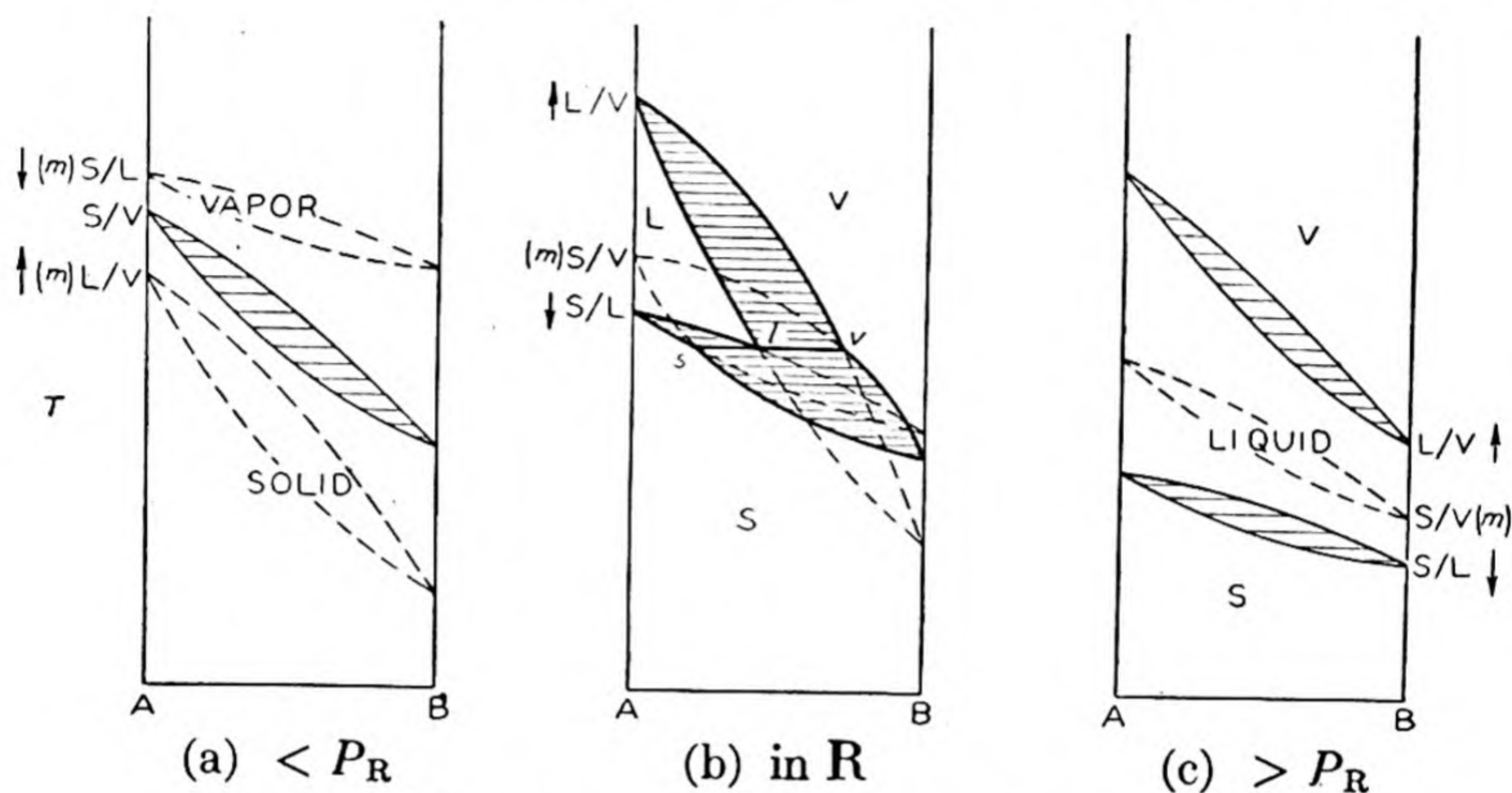


FIG. 3-11. Isobars of Fig. 3-9.

at equilibrium of two phases neither of which is on the plane of the section, which represents the composition of the mixture of phases. Along the curve xy the system is in three phases, the curve being a section of the slv tie-lines of Figs. 3-10(b) and 3-11(b).

2. We shall now consider the case of a $P_{max.}$ (or $T_{min.}$) in the S/L and S/V loops; at the same time the L/V loop will be taken to be of the ascendant type, since with continuous (even if not ideal) solid solution, the L/V loop is not expected to be azeotropic. The case of $P_{min.}$ and $T_{max.}$ in the solid-liquid and solid-vapor relations will not be considered at this point but will be referred to later in connection with compound formation (Chapter VII).¹⁴

Now the 3-phase melting point curve will still be continuous from O_A to O_B and will have a $T_{min.}$, but it may have either a $P_{max.}$ or a $P_{min.}$, or neither. This is perhaps best understood by noting that the solid-liquid and solid-vapor relations being considered ($P_{max.}$ and $T_{min.}$) are the result of repulsion in the solid state, tending to a miscibility gap in the solid state (Chapter IV) and finally to the formation of the pure solids as separate solid phases (Chapter V). When this limit is reached, the melting point temperatures are necessarily lowered, if the components remain miscible as liquids, and there must be a $T_{min.}$ in the SLV relations, then called a eutectic, with two separate solid phases. But, if, as in the system salt (component A)–water

¹⁴ For detailed exposition of the $P/T/c$ relations in a system involving T -minima and P -maxima in all three phase transition loops, see E. Jänecke, *Z. phys. Chem.*, **A182**, 413 (1938).

(component B), the vapor pressure is lowered from O_B to the eutectic and either raised or lowered from O_A to the eutectic, the pressure of the eutectic may be intermediate or even a minimum between O_A and O_B despite the fact that there will always still be a $P_{max.}$ and a $T_{min.}$ in the solid-vapor relations.

Fig. 3-13 represents the case in which the pressure of the SLV equilibrium is always intermediate between O_A and O_B . The line $m_l(s = l)$ is the projection of the $T_{min.}$ or $P_{max.}$ of the S/L loop. The line $m_v(s = v)$ is the projection of the $T_{min.}$ or $P_{max.}$ of the S/V loop. These lines will not meet at the intersection of the three loops, since it is not to be expected that the three phases, s , l , v , have the same composition except at a triple point of a one-component system.

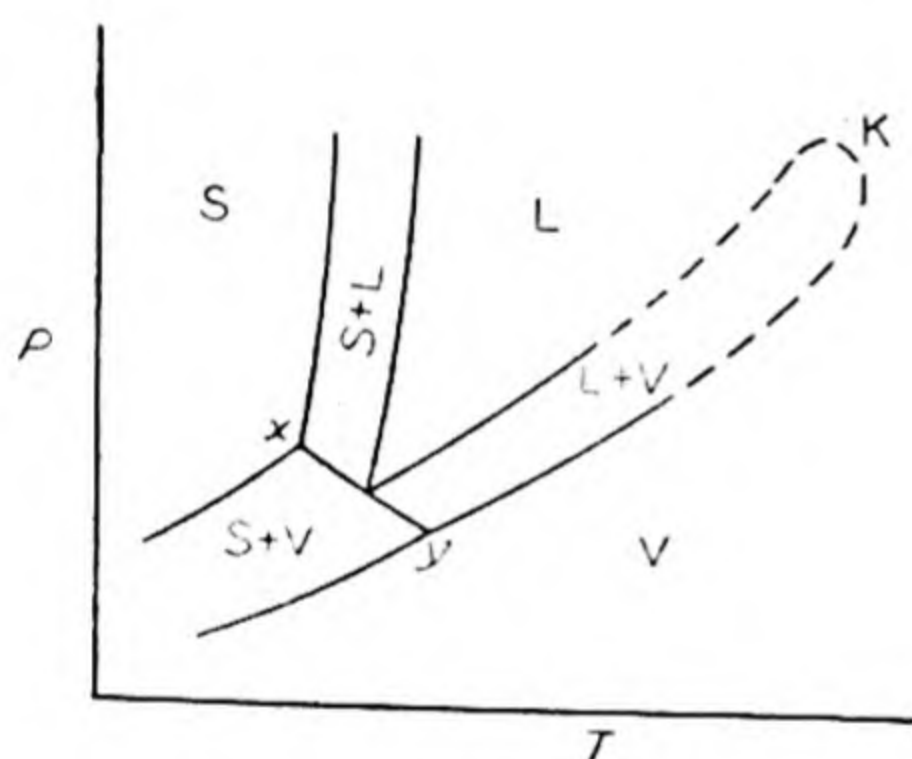


FIG. 3-12. Isopleth of Fig. 3-9.

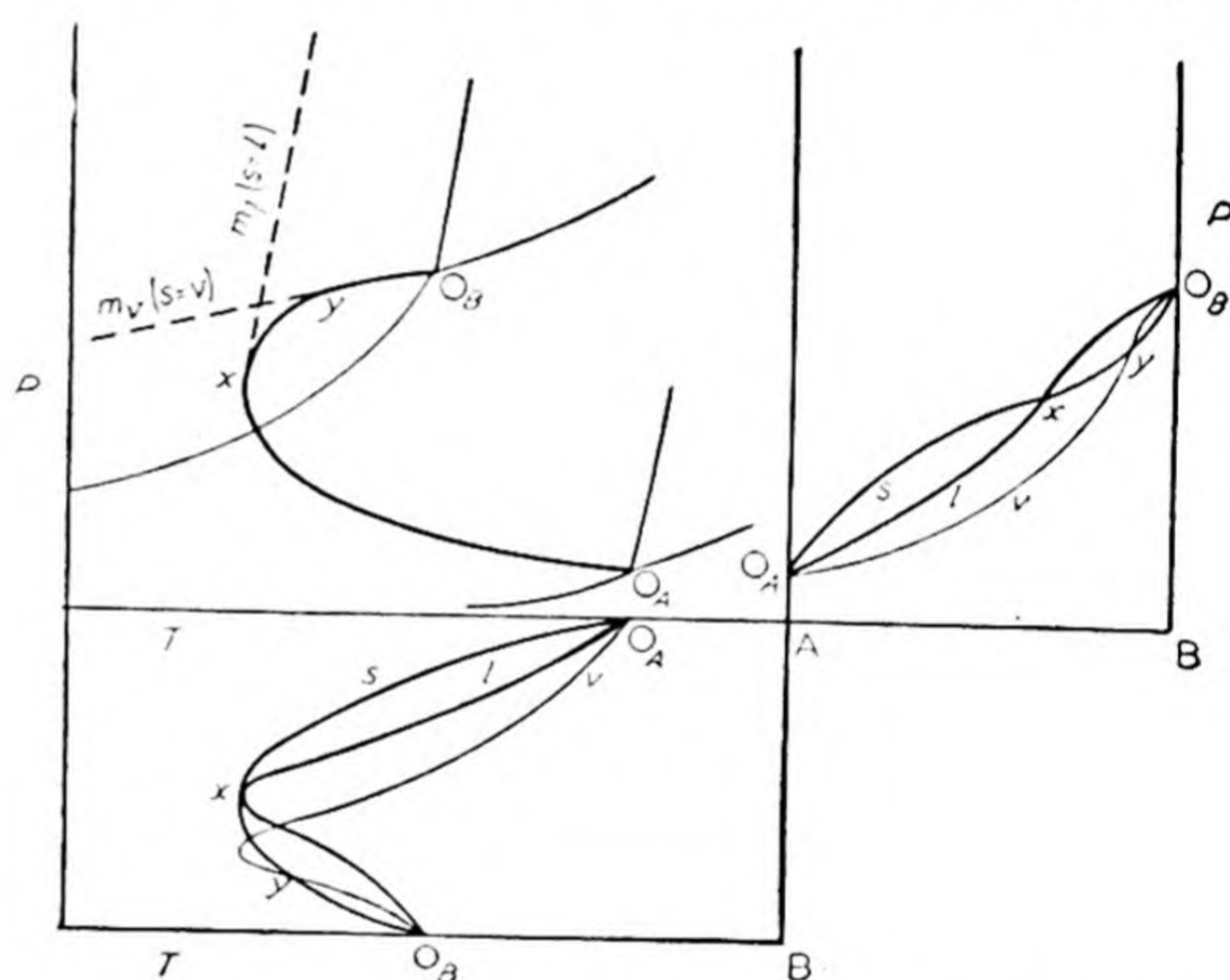


FIG. 3-13. Relations with minimum melting point.

Although, therefore, the s , l and v curves will be continuous from O_A to O_B , they will show certain complexities relative to the points x and y , which are *singular points* of the system. Point x is the temperature minimum of the SLV equilibrium, at which $S = L$ in composition, or the lower extremity of the m_l line of Fig. 13. Point y is neither a minimum nor a maximum of the 3-phase equilibrium, but merely a point in the SLV system at which $S = V$ in composition, and hence at which the order of the compositions of the three coexisting phases undergoes a change, as seen in the P/c and T/c projections. The curves m_l and m_v are 2-phase equilibria univariant-by-restriction, like the azeotropic LV equilibrium discussed in Chapter I, section H. When each meets the continuous 3-phase equilibrium SLV, between O_A and O_B , there consequently occurs, at x and y respectively, a singular point involving a non-critical equality. This will be called a singular point of type m , since it involves the crossing of a 3-phase equilibrium with a maximum or minimum of a 2-phase loop; other examples will be met

later, in Chapters VII and VIII. (A second type, k , of singular point, involving critical identity of two phases in a 3-phase equilibrium, will be introduced in Chapter IV.) Although x is a $T_{min.}$ of the 3-phase equilibrium, the important and general characteristic of this type of singular point is the change in the order of the three phases in respect to composition. If, as

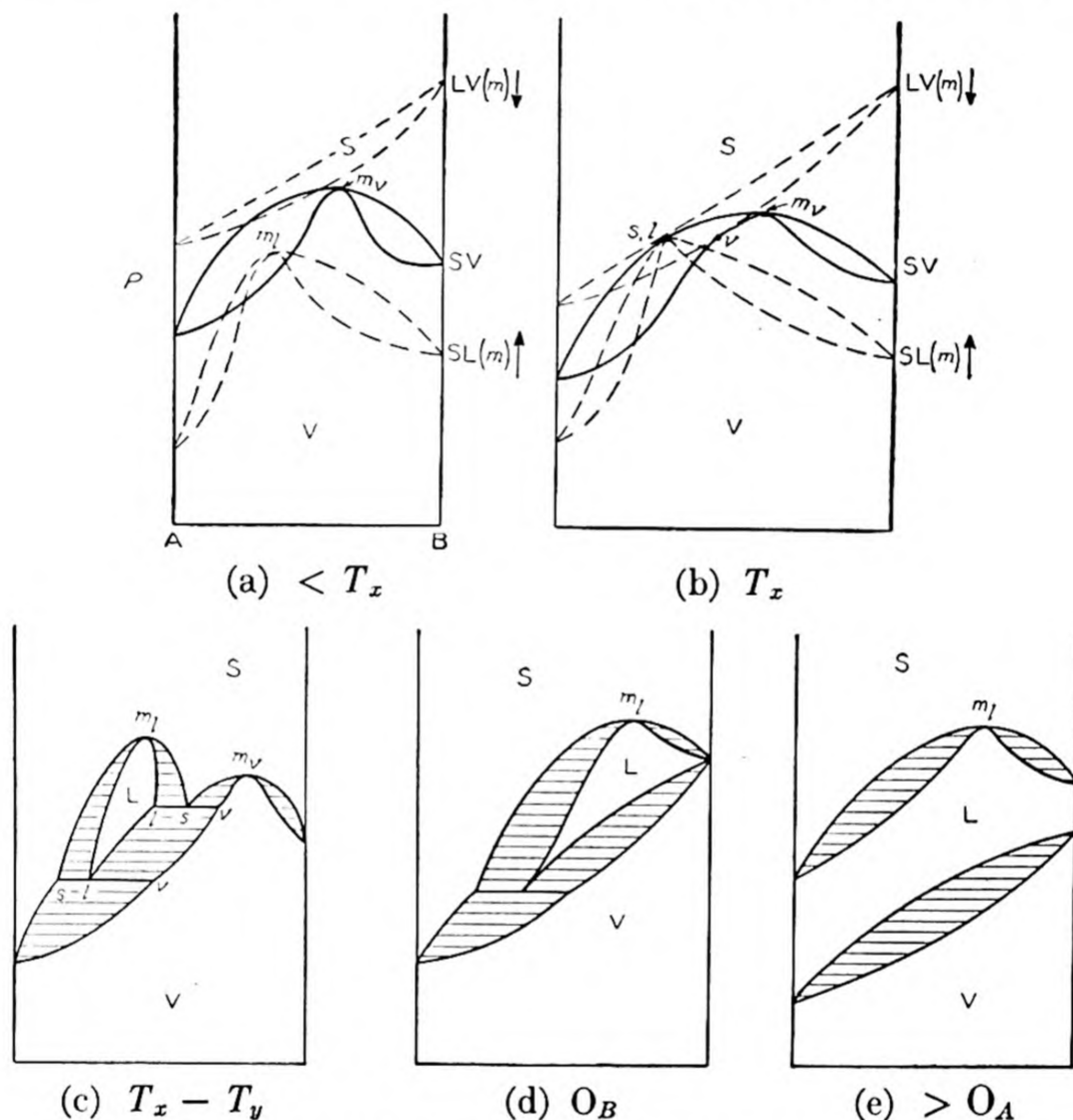


FIG. 3-14. Isotherms of Fig. 3-13.

here assumed, the L/V loop is ascendant, the composition of the vapor is always on the B side of the liquid, whether or not the solid phase is involved in the equilibrium. But the order of solid and liquid and that of solid and vapor must change at the azeotropic points, the first at x , therefore, and the second at y . As seen in the P/c and T/c projections, the order is (always in increasing B content): slv from O_A to x , where s and l have the same composition (on the line m_l); lsv from x to y , at which point, on the line m_v , s and v have the same composition; and lvs from y to O_B .

The relations will be elucidated with some isotherms, Fig. 3-14. Below T_x , we have Fig. 3-14(a). A stable, 3-phase tie-line, that for the point x of Fig. 3-13, for slv , with s and l having the same composition, appears

when the vaporus of the L/V loop touches, at point v in Fig. 3-14(b), the vaporus of S/V, to the left of m_v , while at the same T and P , m_l , or the maximum of S/L, touches simultaneously, at point s , l in Fig. 3-14(b), both the solidus of S/V and the liquidus of L/V. A stable liquid area appears at m_l at T_x , but the m_v maximum for the same T , a 2-phase equilibrium, is on a separate curve, so that just above T_x we have Fig. 3-14(c). The progression of the lower of the 3-phase tie-lines of Fig. 3-14(c), or slv , to O_A is the same as that in Fig. 3-10(b). But as the upper one, lsv , progresses toward O_B , it first incorporates the maximum m_v of the adjoining SV equilibrium, effecting a change in the order of the phases to lvs , since O_B must be approached with falling P at O_B itself. The sequence of relations involved is shown in Fig. 3-15. Finally, at O_B and above O_A , we have Figs. 3-14(d) and (e).

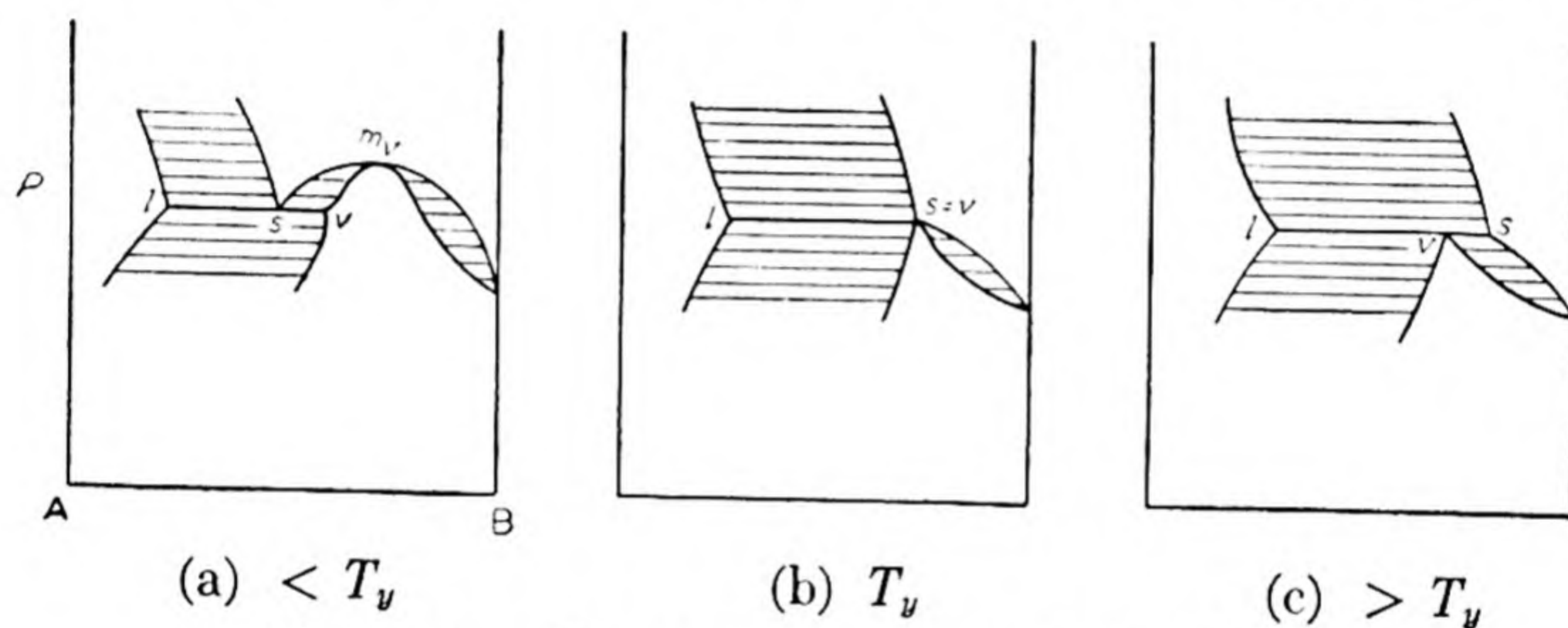


FIG. 3-15. The singular point y of Fig. 3-13.

The T/c projections forming part of Fig. 3-9 and Fig. 3-13, showing the curves of the condensed phases alone, without the vapor curve, are sometimes called the **condensed system**, or the **condensed diagram** of the system. The condensed diagram, then, is a T/c plot of the equilibrium of condensed phases in presence of vapor or, therefore, "under the pressure of the system," but in which the composition of the vapor is not recorded. It is theoretically a projection, on an α -dimensional diagram (a plane for a binary system), representing condensed phase equilibria (S_1S_2 , SL , L_1L_2 , etc.) under the pressure of the system itself, the pressure being therefore variable but not recorded. The true condensed diagram then records determinations of T/c relations of the closed, isolated system under its own vapor pressure as total pressure, in which, however, no record may have been made either of P or of the vapor composition or of both. When the vapor pressure of the system in these equilibria is higher than atmospheric, as in the system $HCl-H_2O$ at the HCl end, the determinations must be made in a closed system. But when the vapor pressure is lower than atmospheric, the determination is often made in the open. The T/c determinations made in the open bear the same relation to the true condensed T/c

diagram that the normal melting point of water bears to its triple point and may be called the normal condensed diagram. The agreement between the two sets of observations again depends on the two factors — solubility of air in the system, and effect of the excess of mechanical pressure upon the equilibria of condensed phases. Since these effects may often be expected to be very small, the determinations are sometimes carried out in a closed system, with air enclosed. Then if the temperature is changed after sealing, the total P itself changes, but its effect on the condensed equilibria is ignored, the result being something between a true and a normal condensed diagram.

Chapter IV Miscibility Gap in Phase 1

(Solid or Liquid)

A. General Relations

A **miscibility gap (MG)** is a 3-dimensional spheroidal region in P, T, c , in the volume or space representing a solution (solid or liquid) of the binary system, within which the system is unstable as a single phase, splitting into two mutually saturating, conjugate solutions. The outline of a miscibility gap in the solid state is shown in the projections of Fig. 4-1.

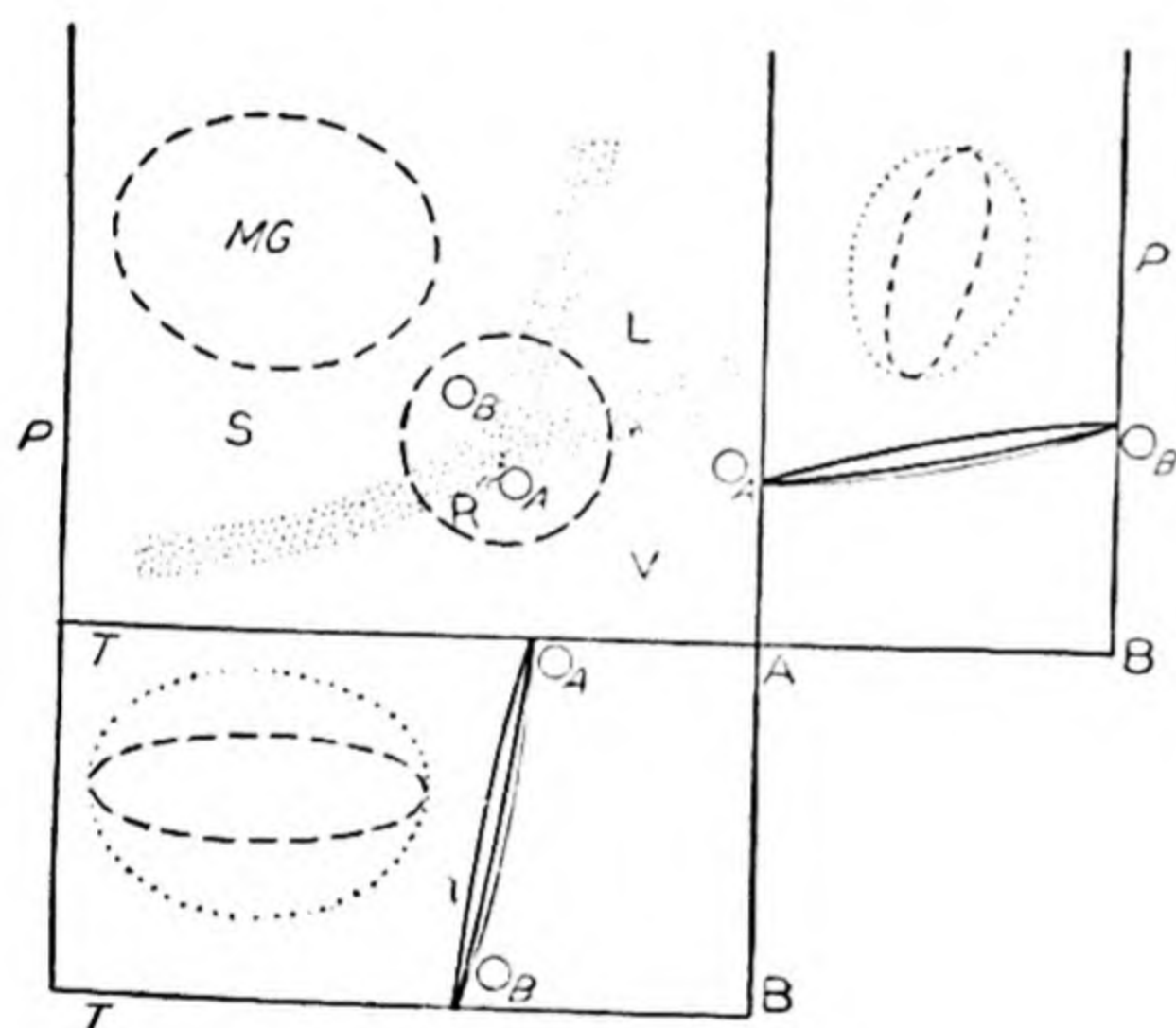


FIG. 4-1. Miscibility gap (MG) in solid state.

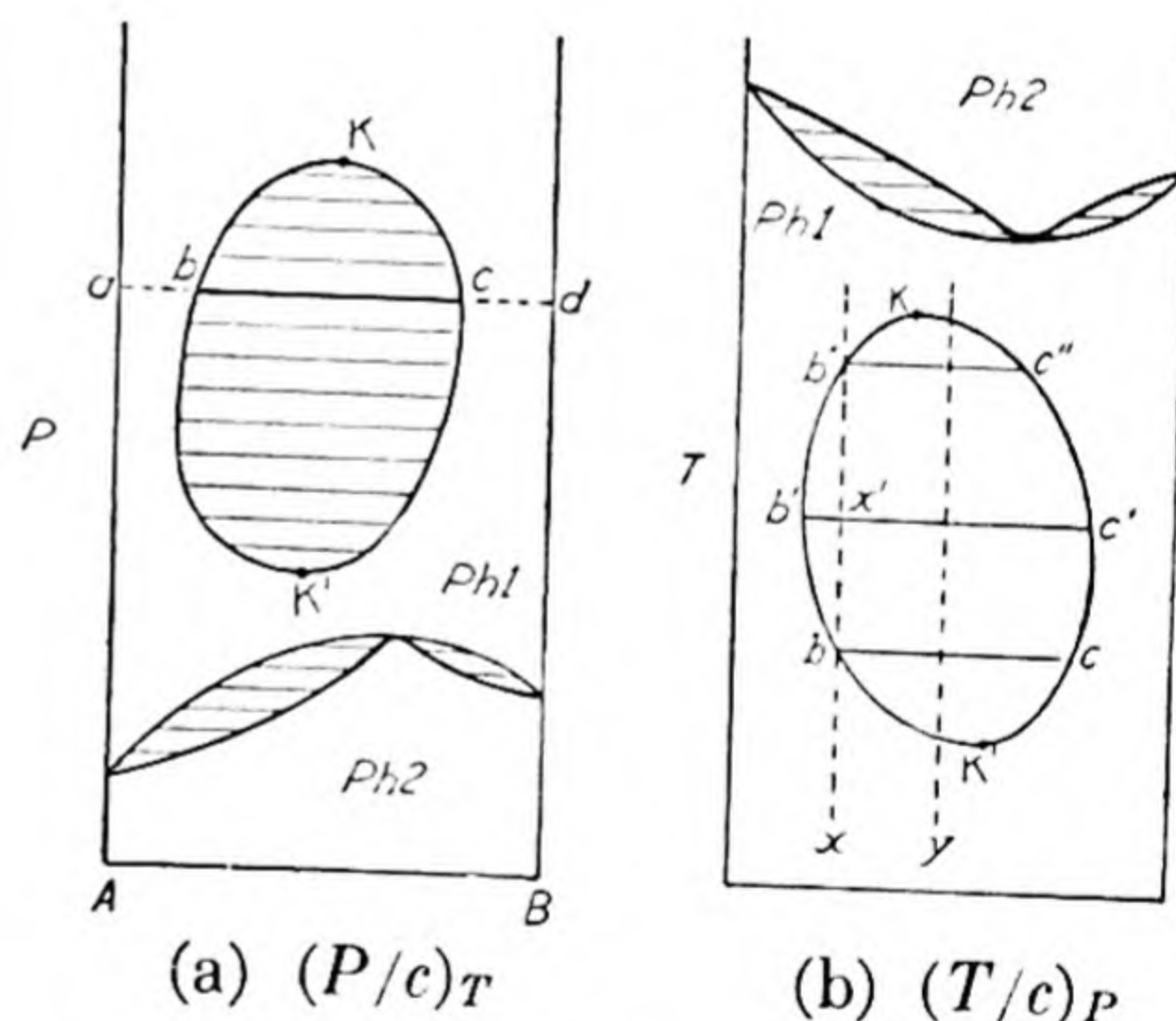


FIG. 4-2. Sections of miscibility gap

Complexes with values of P, T, c falling in the miscibility gap exist, at equilibrium, as two conjugate solutions, then, with compositions given by the ends of tie-lines which fill the MG normal to the P/T projection, and the extremities of which generate the closed, spheroidal surface of the MG .

Fig. 4-2 shows the cross-sections of a miscibility gap, which may be considered to be lying either in the solid or in the liquid state. At each T there is an upper and a lower **critical solution pressure** (K and K'), and at each P an upper and a lower **critical solution temperature** (K and K'); these are also called **consolute points**. As these points are approached, the isobaric, isothermal tie-lines contract, vanishing to points. If the solution x , in Fig. 4-2(b), is heated, at constant P , it remains a single phase

(liquid or solid solution as the case may be) until the curve of the *MG* is reached, at point *b*; at this *T* an infinitesimal amount of solution *c* in the same state appears. If the heating is continued and equilibrium is maintained, the compositions and the proportions of the conjugate solutions are always given by the tie-lines; at some mid-point, for example, the quantities of the phases *b'* and *c'* will be in the ratio $x'c'/b'x'$. Eventually the *c* phase again diminishes and finally disappears with the composition *c''*, leaving *b''* alone, which then remains homogeneous on further heating. If the composition is *y*, between *K* and *K'*, it is the original or *b* phase that finally disappears when the conjugate curve is again cut, on the right of *K*.

If *B* is added to *A* at constant *P* and *T* (Fig. 4-2(a), point *a*), a single solution is formed until the concentration of *B* reaches the value *b*; at this point further addition of *B* causes a second phase to appear, with the composition *c*. The compositions of the two conjugate solutions now remain constant while their proportions change, as more *B* is added. When the total composition reaches *c*, the original phase will have vanished, and between *c* and *d* there is again a single solution.

If a 2-phase system with total composition *K*, Fig. 4-2(b), is taken, the conjugate phases change in composition and ratio, as already explained, as the system is heated. As point *K* (the upper critical solution *T* at the *P* of the diagram) is approached, these conjugate solutions become identical both in composition and in quantity. As any such critical point is approached, the "law of the rectilinear diameter" of Cailletet and Mathias may be applied for the determination of the composition of the critical solution *K*, as suggested by Rothmund for liquid-liquid systems.¹ If the mean densities of the conjugate layers (or, as a substitute, the mean compositions) are plotted against *T*, they should, if the law is applicable, give a straight line, at least near the critical point, passing through the point. Point *K* is not expected to have the same composition as *K'*, at the lower critical solution temperature at this *P*. Solutions on the right of *KK'* are called the *B*-rich layer; those on the left, the *A*-rich solution. In experiment the layer with the lower density will lie upon the other, and we refer to the upper and lower layers respectively; but in some cases the relation of the densities may change between *K* and *K'*, reversing the position of the phases, as occurs for the system nicotine-water at 90°C.²

The outline of the *MG* in the *P/T* projection of Fig. 4-1 is the projection of the **critical curve** or **consolute curve** generated by the points *K*, *K'*, and it is not a curve of constant composition. This critical curve, shown as

¹ V. Rothmund, *Z. phys. Chem.*, **26**, 433 (1898).

² C. Hudson, *Z. phys. Chem.*, **47**, 113 (1904). For further examples, both binary and ternary, see P. Mondain-Monval and J. Quiquierez, *Bull. Soc. chim.*, **7**, 240 (1940).

a dashed curve, is furthermore not coincident with the outline of the gap itself, on the P/c and T/c projections (also in Fig. 4-1).

If the MG , as in Fig. 4-1, does not reach and touch any phase transition equilibrium of the system, it is known as a (completely) closed MG and it has no effects on the phase transition relations already discussed in Chapter III; this is seen in the isothermal and isobaric sections of Fig. 4-2. The conjugate relations in the solid state below the melting point curves are, of course, very difficult to investigate; in some cases the information may be obtainable through the study of ternary systems in which the third component is a liquid solvent forming no additive compounds with the two solids.

Like the transition loops (S/L , S/V , L/V) the MG is a 2-phase, tie-line equilibrium, a space in 3-dimensional and an area in cross-sectional representation. But the phases connected by the tie-lines of the MG , or the conjugate phases, are not only always in the same state of aggregation, but are also merely different compositions of what is structurally the same phase, which is continuous in three dimensions around the gap. Its surface is not a "phase transition" surface in the sense of the loops previously discussed. The maxima and minima in P/c and in T/c do not involve a meeting of two curves, and their meaning is different from that in Fig. 3-4. When the tie-lines vanish to points at the maximum or minimum of a MG , the phenomenon is a critical one in that the two coexisting phases not only have the same composition but are identical in all properties and even in their quantities, whereas at the extremities and at the maximum or minimum of a transition equilibrium, where the tie-lines also vanish to points, the phases are distinct except in composition, and their ratio depends on volume and heat content.

In either case, however, we speak of **solubility**, although the nature of the phenomenon may be very different. The calculation of the "solubility curve" of a solid in a liquid is the calculation of a freezing point curve, in general a problem involving change of state (or at least of polymorphic forms in the same state); and the question is the effect of a foreign substance on a transition temperature or pressure. In the problem of the mutual solubility of two substances in the same state, on the other hand, we are concerned with miscibility *per se*, depending on dimensional differences between them, internal pressures, lattice energies, etc. Nevertheless there may be in some cases an overlapping between the two kinds of solubility curves, as we shall find in the case of the liquid-liquid solubility curve which, at the critical region of the $L \rightleftharpoons V$ transition, may become continuous with the LV solubility or transition curve. "Saturation," then, which is here the essential idea of solubility, will simply be taken to mean the heterogene-

ous equilibrium between two phases, regardless of whether they are in the same or different states of aggregation, of whether or not they may be considered continuous around some critical point, and of whether or not they are both variable in composition. Any phase surface of the $P/T/c$ diagram is accordingly called a solubility surface; all phase transition surfaces are solubility surfaces, but not all solubility surfaces represent phase transitions in the sense of involving a latent heat of transition.

B. Intersection of the Miscibility Gap with Phase Transition Loops

We now consider the intersection of a MG in $Ph\ 1$ with the transition loop $Ph\ 1/Ph\ 2$, but without including the melting region R . In Fig. 4-3 the P/T projection shows a MG in the solid state penetrating the S/V loop

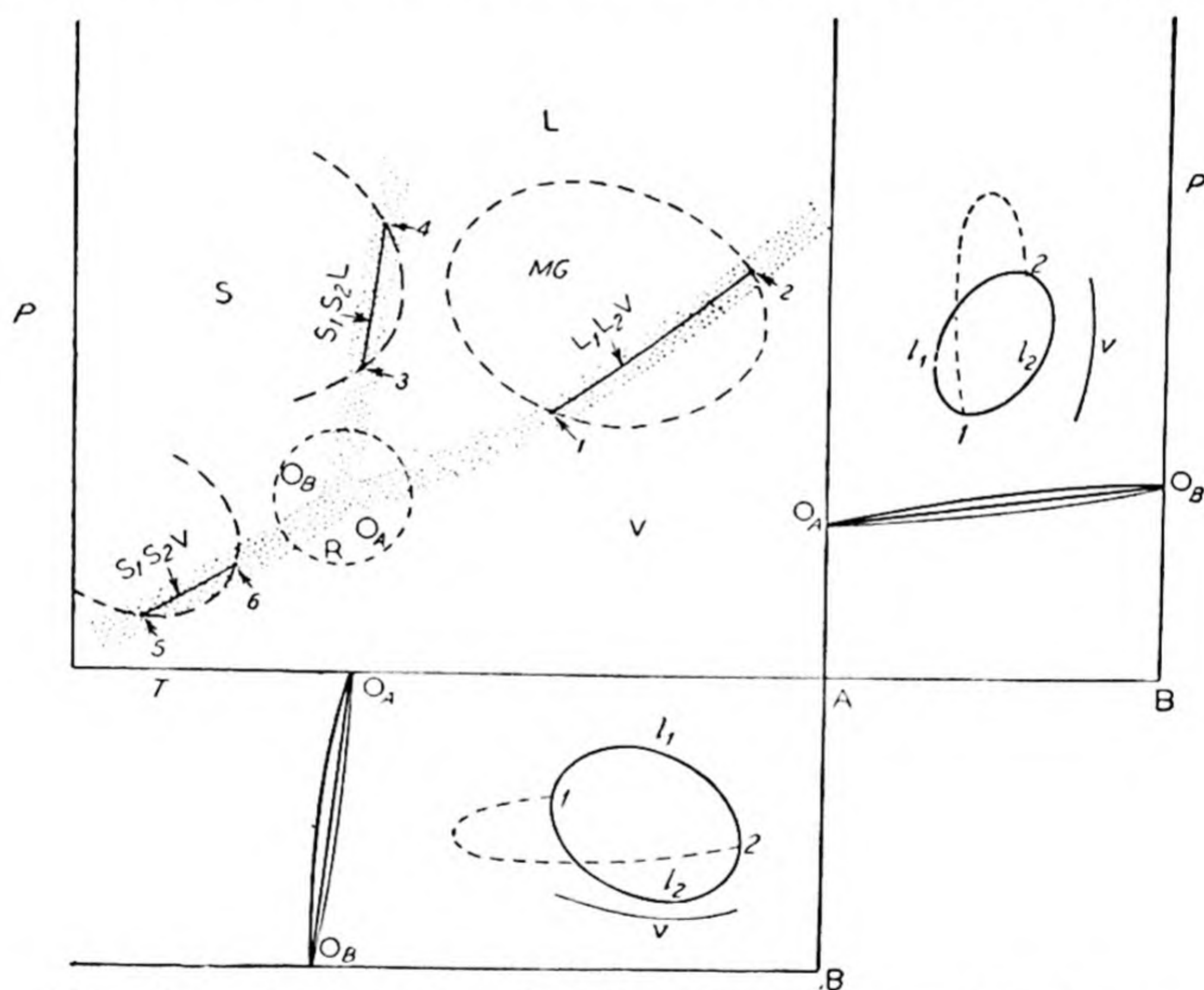


FIG. 4-3. Intersection of MG with phase transition loop.

between points 5 and 6; it also shows a solid MG penetrating the S/L loop between points 3 and 4, and a liquid MG penetrating the L/V loop between points 1 and 2. What we shall have to say applies to any of these intersections, as parallel cases of the transition $Ph\ 1 \rightleftharpoons Ph\ 2$. But since the most familiar of these intersections, as function of both P and T , is that involving the liquid MG and the L/V loop, we shall use this as the specific text, keeping in mind always that the relations may be generalized to the other cases by the simple substitution of the general terms $Ph\ 1$ for L and $Ph\ 2$ for V .

The P/c and T/c projections of Fig. 4-3, therefore, show only the relations pertaining to the liquid MG . The "submerged" portion of this

MG between points 1 and 2, and lying within the vapor space, is metastable. The continuous lines 1-2, 3-4, 5-6, are 3-phase, univariant equilibria, L_1L_2V , S_1S_2L , S_1S_2V , respectively, equilibria representing the intersection of the MG with a transition loop. The intersection curve (ellipsoid) for the equilibrium L_1L_2V , between points 1 and 2, is then shown as a closed continuous curve above the melting point (SLV) equilibrium in the accompanying P/c and T/c projections of the figure. This closed curve is not the outline of the MG as in Fig. 4-1, but only the *intersection curve* for the penetration of the L/V phase transition loop by the liquid MG . Between the points 1 and 2 the 3-phase equilibrium involves liquid L_1 (A-rich) on the A side of points 1 and 2, a conjugate liquid L_2 (B-rich) on the B side of these points, and a vapor phase which in the present case is assumed to have a composition always between L_2 and pure B. For part of the range of the intersection curve, or somewhere between points 1 and 2, the composition of the vapor may run between L_1 and L_2 . Similarly the 3-phase equilibrium between points 3 and 4 involves the solid solutions S_1 (A-rich) and S_2 (B-rich), and a liquid phase. Finally, the critical solution curve KK' (or the curve $L_1 = L_2$) is shown on all three projections, running from point 1 to point 2.

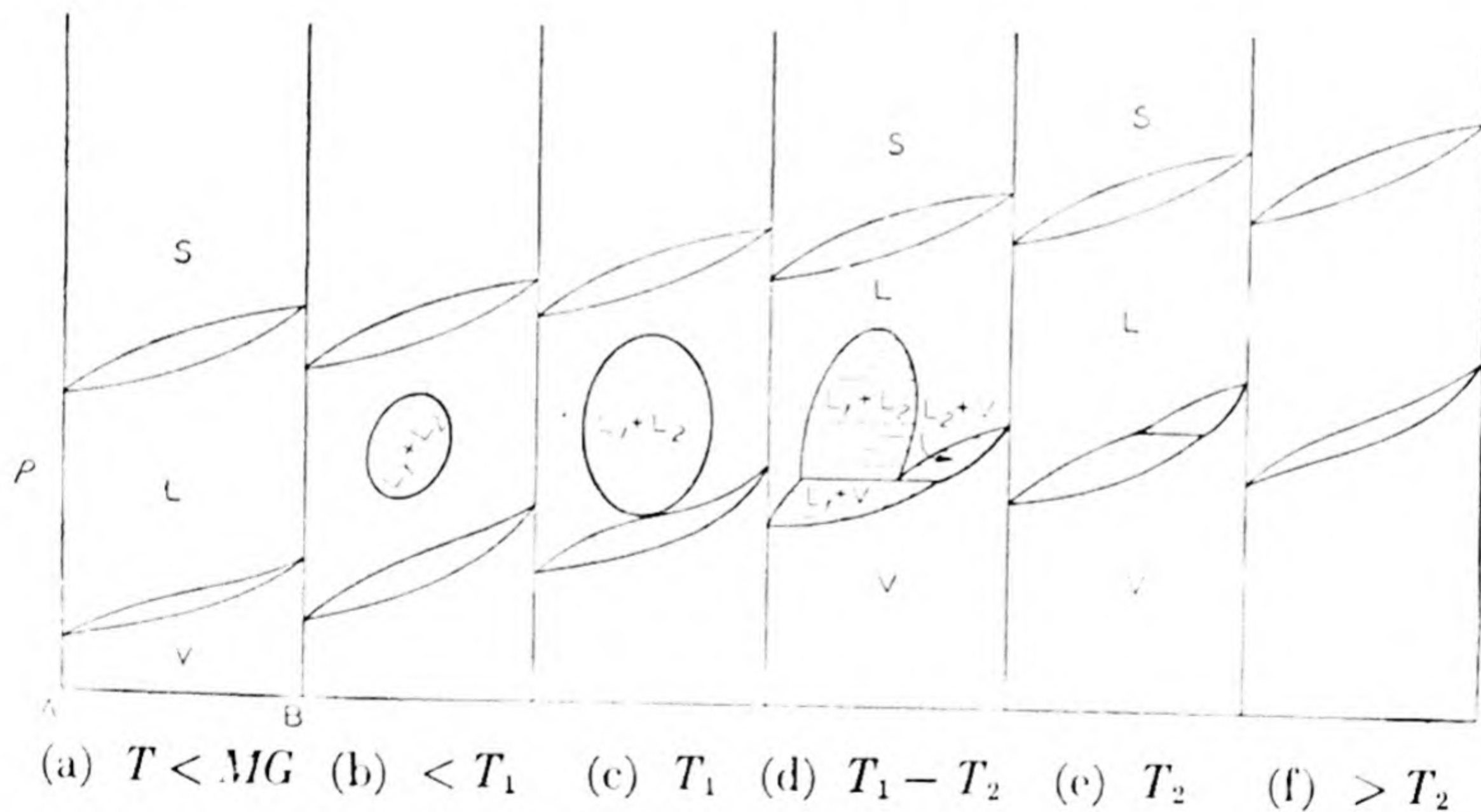


FIG. 4-4. Isotherms of Fig. 4-3.

The relations represented in Fig. 4-3 (for the liquid MG) may be analyzed more fully by the series of isotherms shown in Fig. 4-4, in which both the S/L and the L/V loops are assumed to be of the simple ascendant type. If these six diagrams are turned upside down, reversing the order of the states and the slope of the loops, they would constitute the corresponding set of isobars in the order $P > MG$, $> P_2$, P_2 , $P_1 - P_2$, P_1 , $< P_1$.

The special points 1 and 2 are singular points, with particular values of

T , P , c , where the critical curve, KK' , of the MG intersects the phase transition loop. They are 3-phase *critical solution points*, singular points, type k , at which two liquid phases become identical in all properties while in equilibrium with a vapor of different composition, at points 1 and 2. The points 3, 4, 5, 6 of Fig. 3 are also such singular critical solution points, type k ; at points 5 and 6, two solid phases become identical while in equilibrium with a vapor of different composition, and at points 3 and 4 the two solid solutions become identical while in equilibrium with a liquid phase of different composition.

A singular point of type k marks the termination of a 3-phase invariant equilibrium (such as L_1L_2V) at its intersection with a critical curve (here $L_1 = L_2$). A singular point type m , on the other hand, is the intersection of a 3-phase univariant curve (again such as L_1L_2V) with a non-critical equality curve, which may be either an azeotropic curve, like that generated by point m of Fig. 4-7(b), or a curve of "congruent transition," to be discussed in Chapter VII; it is in either case the intersection with a curve representing the maximum or minimum of T or P for a 2-phase equilibrium. The singular point type m , then, is not a termination of the 3-phase equilibrium, for this proceeds smoothly and continuously through the point, which marks simply the reversal of the order of the two phases involved in the equality curve.

On the isobars (or isotherms) of Fig. 4-4 the critical solution points represent the detaching of the 2-liquid area from the transition loop, as in Fig. 4-4(c), or the vanishing of the MG from the transition loop, as in 4-4(e). In either case they are points of contact of the MG with the liquidus of the L/V loop, the gap being submerged or metastable in Figs. 4-4(e, f), and stable (that is, in the actual liquid area) in Figs. 4-4(b, c). Such contact may occur on either side of a minimum or maximum of the transition or L/V loop. Since the contact involves the critical curve of the MG , where $(dc/dP)_T = 0$ or $(dc/dT)_P = 0$, the liquidus curve, tangent to the MG at the contact, must become highly flattened preparatory to the contact. The contact is not expected to occur either at a minimum or at a maximum of a phase transition loop, since this would constitute a 3-phase equilibrium with two "equality restrictions," namely, critical identity of two solutions and identity of composition of two phases in different states, and according to equation 14 of Chapter I this would mean $F = -1$ or impossible. Perhaps "infinitely unlikely or improbable" is the better expression. The critical point of the MG and the point of maximum pressure on the LV curve — on an isotherm — are points (dimensionless) on continuous curves. Hence, the chance of their meeting, without a thermodynamic necessity therefor, is practically zero.

All the contacts (points 1-6 of Fig. 4-3) therefore occur on parts of the

transition loops other than maxima or minima, so that we expect the following types of isothermal sections, for example, on the L/V loop (Fig. 4-5). For part of the range between the ends of the 3-phase equilibrium, points 1 and 2 of Fig. 4-3, Type II may, with change of T , become Type IV, in which the vapor pressure of the 3-phase (L_1L_2V) equilibrium is a maximum for the isotherm, by engulfing the maximum of Fig. 4-5(b) through trans-

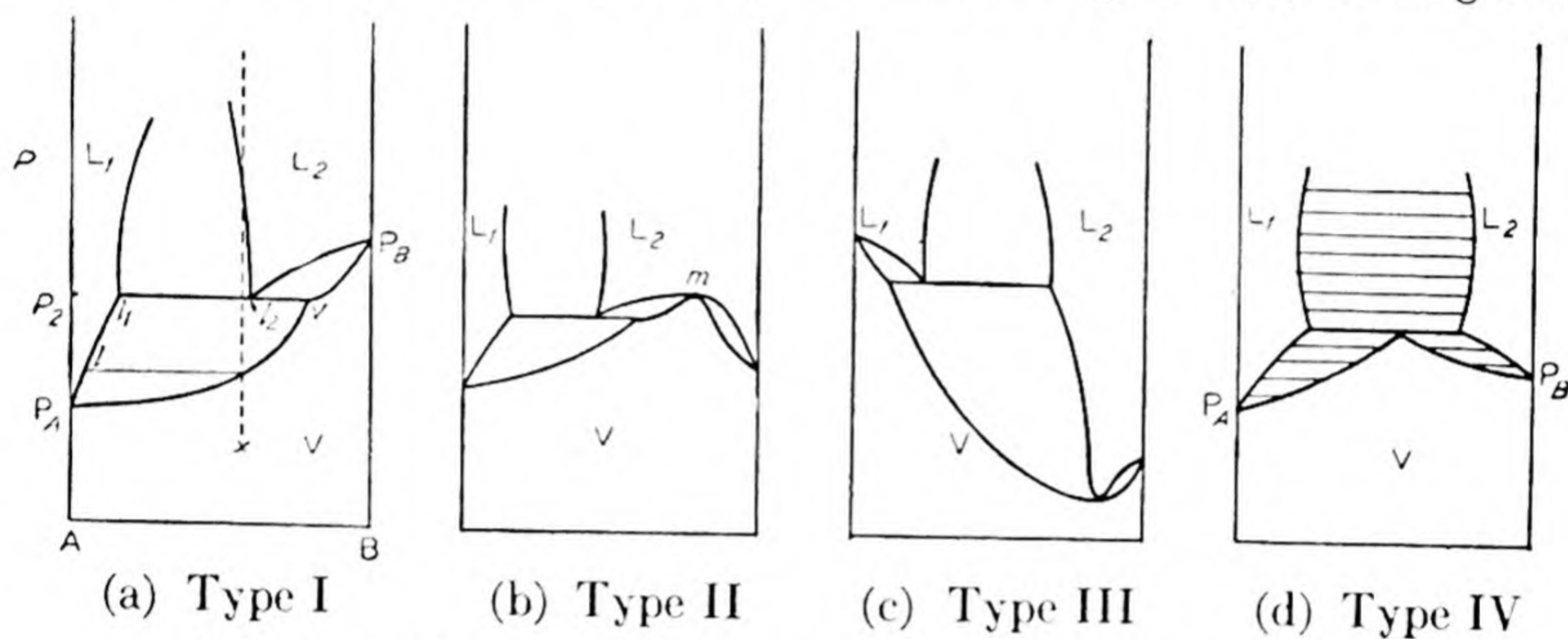


FIG. 4-5. Vapor pressure relations for 2-liquid systems.

formations identical with those of Fig. 3-15. The 3-phase equilibrium L_1L_2V of Type II, in other words, meets the maximum, m , of the LV equilibrium, or it crosses the azeotropic LV curve, at a singular point of type m ; and at this point the order of the three phases changes, then, from L_1L_2V to L_1VL_2 as in Fig. 4-5(d). Furthermore, the maximum of Type II and the minimum of Type III may disappear, with change of T , so that these types may change to Type I.

Büchner³ stated as an empirical rule that if the boiling point of A is higher than that of B by 100° or more, the system is of Type I, while if the difference is less than 100° , it would be of Type II or IV; he also suggested, as "theoretically sounder," the rule that Type I results if the critical temperature of A is equal to at least 1.4 times that of B. The system ethyl acetate-water,⁴ with boiling points 77° and 100° respectively, as also the system aniline-water,⁵ belongs definitely to Type IV. Phenol-water, with boiling points 182° and 100° , may be either Type I or Type II.⁶

The vapor pressure of the 2-liquid system at any T (that is, the pressure of the 3-phase tie-line of Fig. 4-5) may therefore be the maximum, as in Fig. 4-5(d), but not the minimum of the isotherm. Moreover, since the vapor pressure of the 2-liquid system must be higher than that of an ideal

³ E. H. Büchner (Ref. P), Vol. II, part 2, p. 35.

⁴ R. W. Merriman, *J. Chem. Soc.*, **103**, 1790 (1913).

⁵ J. Griswold, D. Andres, E. F. Arnett and F. M. Garland, *Ind. Eng. Chem.*, **32**, 878 (1940).

⁶ F. A. H. Schreinemakers, *Z. phys. Chem.*, **40**, 440 (1902).

liquid solution of the composition of either liquid, the composition of the liquid richer in the more volatile component, l_2 in Fig. 4-5(a) or l_1 in Fig. 4-5(c) must lie above the straight line joining P_A and P_B in the isothermal diagram; no similar generalization, however, may be made with regard to the composition of the vapor, v . When the vapor pressure of the 2-liquid system is the maximum of the isotherm, it cannot be greater than the sum of the vapor pressures, P_A and P_B , of the pure components, a limit reached only in the case of completely immiscible liquids. If the two liquids are completely immiscible, or at least practically immiscible, the vapor pressure of the 2-liquid system is simply the sum of the individual vapor pressures, at any T , and the boiling point is the temperature at which this sum equals the atmospheric P (Fig. 4-6). In "steam distilla-

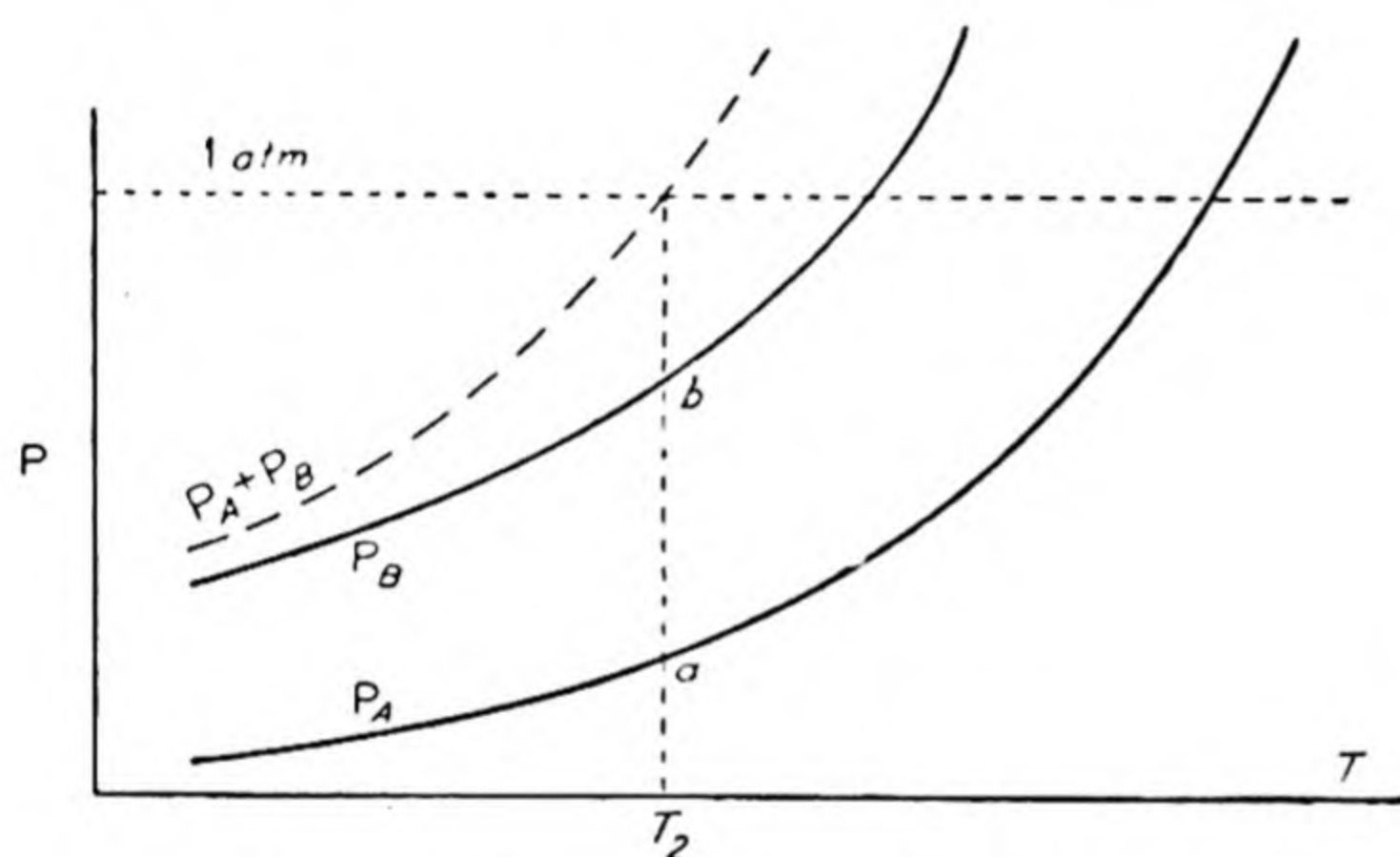


FIG. 4-6. Immiscible liquids.

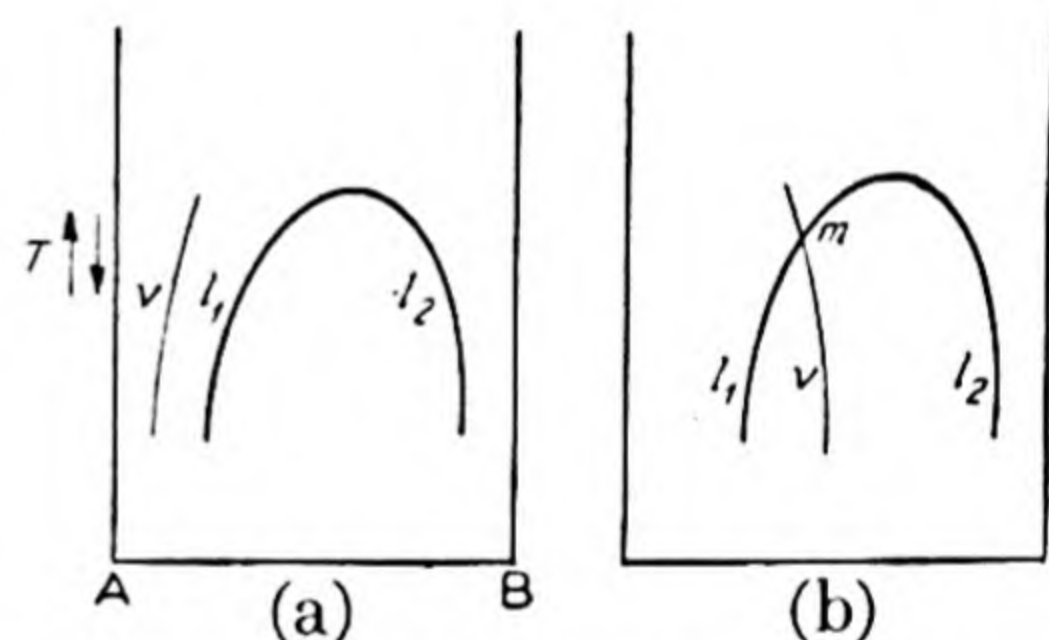


FIG. 4-7. Vapor composition in 2-liquid systems.

tion" of a relatively nonvolatile liquid A, immiscible with water (B), the boiling point is T_2 , and the proportions (molecular) in the vapor will be $A/B = a/b$ (ideally). The boiling point is constant at T_2 until one of the liquids is completely distilled, and then rises to the boiling point of the residual liquid.

The terminal, critical points, 1-6 of Fig. 4-3, at which the MG either disappears to a point, becoming "submerged" or metastable, or detaches itself, as a stable 2-liquid region, from the transition loop, may then be of any of the Types I, II, III, but not IV. In the first three types the composition of the vapor in equilibrium with two liquids may remain outside the range of compositions of the liquids throughout, as in Fig. 4-7(a). In IV the composition of the vapor, which is between the liquids, would then, if it remained so, be the same as that of the two identical liquids at the terminal critical point L_1L_2V , when the MG vanishes or becomes detached; hence this type changes to Type II before a critical point is reached, as in Fig. 4-7(b). The change occurs at the singular point of type m mentioned above.

An example of Fig. 4-7(b) is the system triethylamine–water,⁷ with a lower critical solution point near 18.5° and the crossing, or point m , near 20.5° . It should be noted, of course, that with *Ph 1* for L and *Ph 2* for V, the relations of Fig. 4-7 apply in general. Later, in Figs. 4-10 and 4-13(b), for example, the point m marks the crossing of the liquid curve with the S_2 curve, in the 3-phase equilibrium of two solids + liquid, as the critical solution point $K(4)$ is approached. The equilibrium there starts as S_1LS_2 , Type IV, as it rises from Q, and changes, at point m , to S_1S_2L , Type II.

As explained in Chapter III, the corresponding isobaric sections look like the isotherms simply turned upside down (Fig. 4-8). At the pressure of

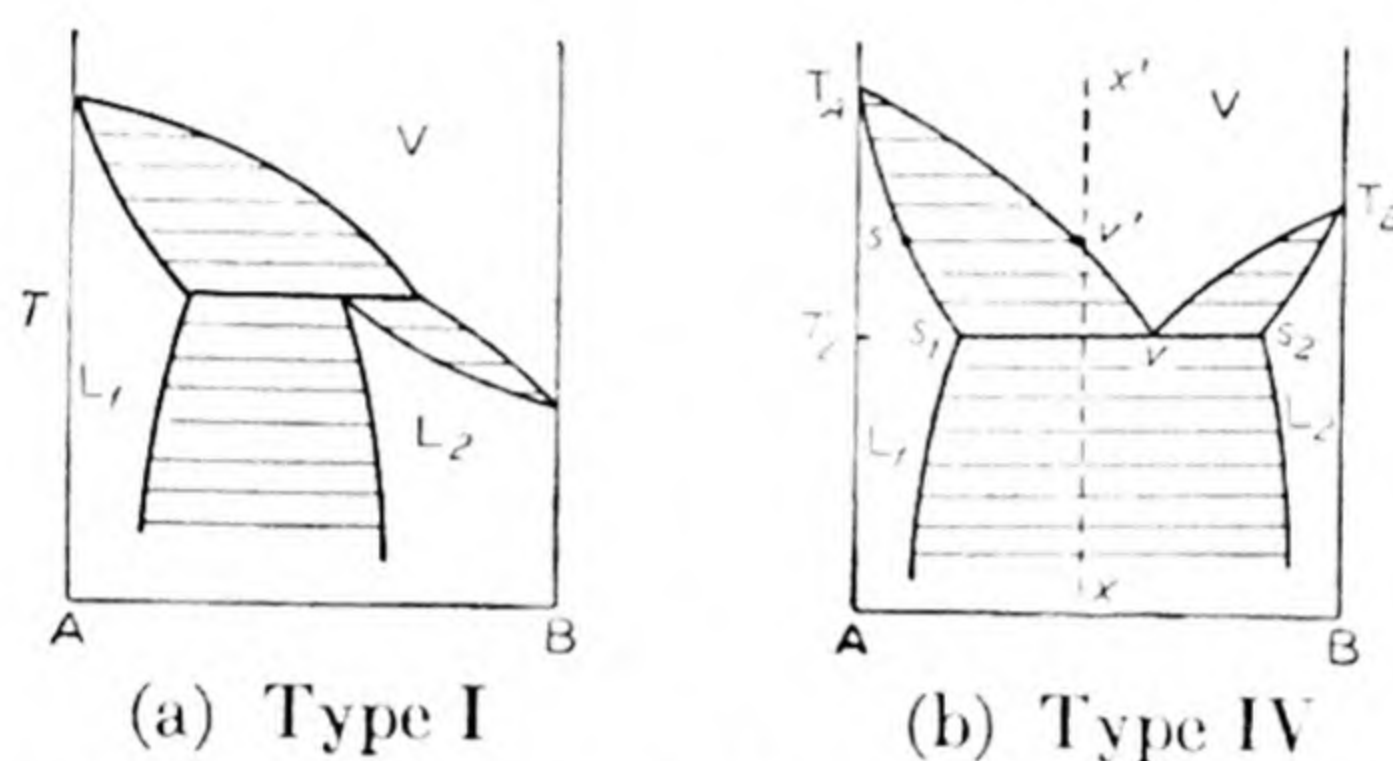


FIG. 4-8. Boiling point relations for 2-liquid systems.

Fig. 4-8(b), the complex x exists in two liquid layers, L_1 and L_2 , which change in composition and proportions, during heating, until the boiling point of the 2-liquid system is reached, T_2 . The 3-phase binary system boils with isobaric invariance, giving off the vapor v , until the liquid L_2 is entirely consumed. Now the boiling point rises along the curve v - T_A and the sample is completely vaporized to the vapor v' at T_v . But if boiling is carried out in the open and vapor is continually removed, the boiling point rises, as usual, toward T_A as a limit. In reverse, x' may be taken as a liquid solution being cooled at constant pressure. At T_v it precipitates solid of composition s' . If equilibrium is maintained during further cooling, the freezing point falls along the curve v' - v , which also gives the composition of the liquid solution in equilibrium with the variable solid solution on curve s' - s_1 . When the temperature T_2 is reached, we have isobaric invariance, and the residual liquid, now of composition v , freezes at constant T leaving a mixture of the solids s_1 and s_2 ; the further changes of the solid solutions, at lower T , are given by the tie-lines of the *MG* below T_2 .

In Fig. 4-5(a), the vapor x , compressed at constant T , forms some liquid l on reaching the vaporus. Below P_2 it then exists as a 2-phase system, $L_1 + V$; at P_2 a second liquid, L_2 , appears, and the system is isothermally

⁷ R. T. Lattey, *J. Chem. Soc.*, **91**, 1959 (1907).

invariant while all the residual vapor, v , condenses to leave a 2-liquid system $l_1 + l_2$, whereupon the pressure may again rise.

The points 1–6 of Fig. 4–3 have already been stated to be singular, critical solution points. Since one of the three phases in such a singular state is not involved in the critical phenomenon, there is no fixed ratio of this phase to the amounts of the critical phases. Hence there is no critical composition or density of the system as a whole, but there is a unique relation between the over-all composition and the over-all density. In the absence of this condition — a particular volume for a particular sample — the 3-phase, critical solution phenomenon is not observed. This is true, of course, even in the absence of the non-critical phase, such as V in L_1L_2V .

If the vapor pressure of the 3-phase univariant system L_1L_2V is lower than atmospheric, it may be studied in the open, and the T/c relations so observed may be plotted as a “normal” condensed diagram, such as Fig. 4–9. Here K gives the composition and T for the critical relation $L_1 = L_2$ observed in open air, presumably at 1 atm P , K the upper, K' the lower, critical solution point, thus observed. For the relation of this diagram to the T/c projection of the system under its own pressure (Fig. 4–3), in which we would identify K' with point 1 and K with point 2, it is necessary first of all to assume that the air has caused no effect on the 3-dimensional relations by dissolving in the liquids. Then since the mechanical pressure can have no appreciable effect on the vapor pressures, Fig. 4–9 will represent, effectively, the isobar of the MG at 1 atm P , presumably somewhat above P_2 of Fig. 4–3.

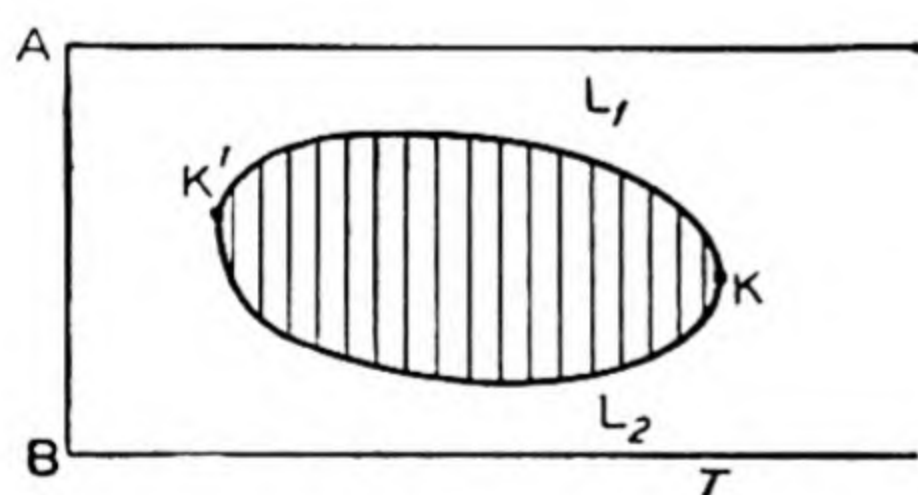


FIG. 4–9. Condensed diagram of MG .

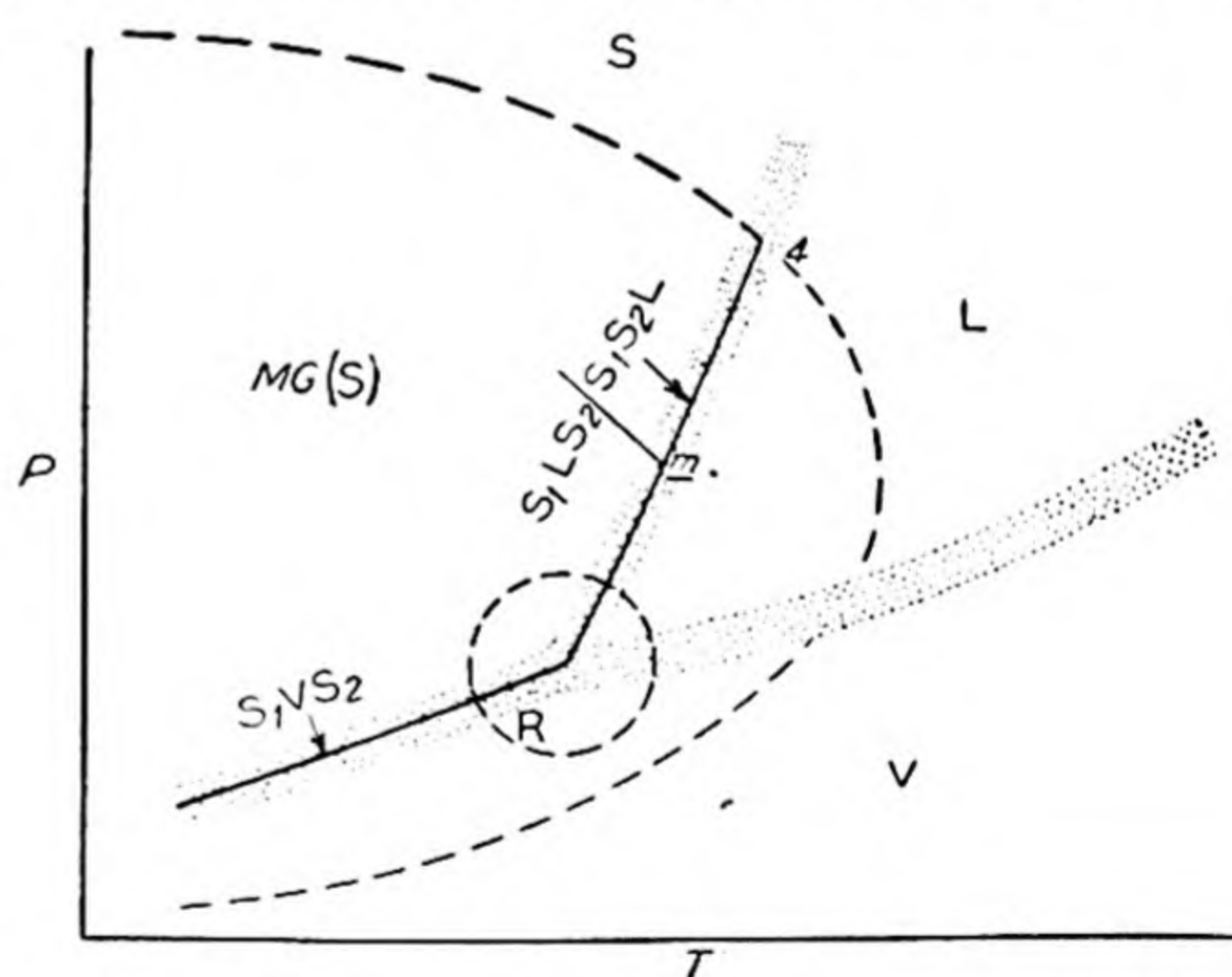


FIG. 4–10. Intersection of MG in solid state with melting region.

When this procedure is applied to curves of transitions of condensed phases (solubility curves in the ordinary sense of a solid in a liquid, or melting point curves), the observed “normal” invariant points may confidently be expected to be very close to the true invariant points of the system, since the effect of one atmosphere (or less) upon the transition temperatures and compositions will generally be negligible. But in a critical solution point

(not an invariant but a singular point) the effect of P may be considerably greater, since it depends on the angle of contact, in respect to both the projection P/T and the projection P/c , between the critical curve KK' of the MG and the 2-phase transition loop involved, at the critical solution point. If the 3-dimensional critical curve KK' is quite perpendicular to the T/c face of the space model, the error will be small. But it is at least possible for the KK' curve to approach one of the critical solution points, such as at point 1 of Fig. 4-3, with a very small P/T slope, and, in addition, to swerve considerably in respect to c as it approaches the point. It may therefore be necessary to have at least approximate values of the derivatives dT/dP and dc/dP , in order to extrapolate from the observed "normal" critical solution point to the true point with accuracy. This, in addition to the difficulty of precise observation, may be one reason for the low reproducibility of some critical solution points. The increase of P over that of point 1 or point 2, in other words, may not only cause a marked change in the "mutual solubility" of the liquids, but may also cause an appreciable change in the proportions required for the critical phenomenon. Under the P of the system itself (P_2 of Fig. 4-3 for the upper consolute point of the equilibrium L_1L_2V), the proportions of the components A and B required to give the critical solution phenomenon are those of point 2 (disregarding the vapor) shown in the P/c and T/c projections of Fig. 4-3. If the experiment is done in the open and if P_a (the atmospheric P) is $> P_2$, the consolute point is now at higher P and lower T , and also at a different liquid composition. If therefore the original proportions, holding at P_2 , are used, we do not observe a critical or consolute phenomenon at all in the open, but merely the appearance or disappearance of one of the liquids, here L_1 . If the proportions are adjusted to give a critical phenomenon at P_a , in the open, they will not in general hold for any other P . If P is high enough, the original proportions for point 2 may fail to show the MG at all, simply because the required proportions are not used.

C. Intersection of the Solid Miscibility Gap with the Melting Point Curves (SLV)

If the MG in the solid state intersects the SLV melting point curves, there arises a quadruple, invariant point in the binary system. In Fig. 4-10 the MG is shown overlapping the melting point region R to such an extent that the MG remains "open" at lower T but becomes "closed" at high P . Since the S_1S_2V and the S_1S_2L relations at terminal critical solution points such as 3 and 6 of Fig. 4-3 are never of Type IV, it will be seen that if these two points barely overlap in the melting point region, the quadruple point is of the **peritectic** type (not the lowest melting point of the binary system,

under its own pressure), the lowest melting point remaining, if present, as in Fig. 3-13 (T/c projection), a minimum in a continuous curved section of the SLV curves.

The T/c projections of the melting point relations will then be as in Fig. 4-11; in 4-11(a) the gap intersects a melting point system of the ascendant type, giving a simple peritectic; in 4-11(b) it intersects a system

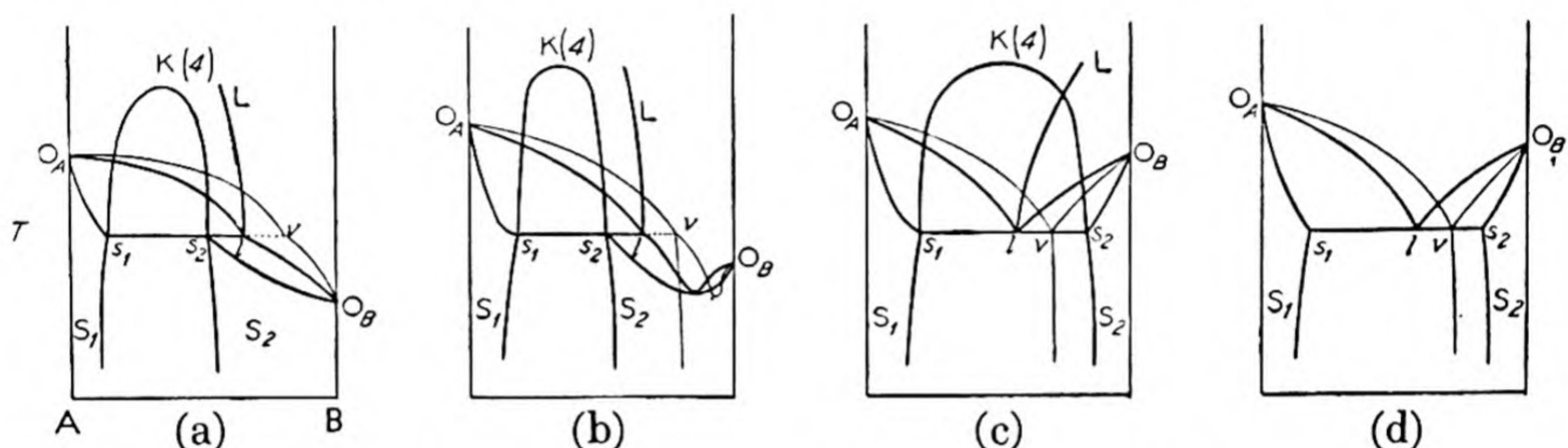


FIG. 4-11. T/c projections of Fig. 4-10.

which still preserves its continuous minimum on the B side of the peritectic; and in 4-11(c) the minimum has been incorporated in the MG so that the quadruple point is now a **eutectic**, the lowest melting point of the binary system, under its own pressure. Experimentally either solid phase in a diagram like Fig. 4-11(c) may be pure, depending on the position and width of the MG . If the S/L equilibrium of Fig. 4-10 is assumed perpendicular to the T -axis, Fig. 4-11(c) becomes 4-11(d). The invariant point s_1s_2lv of Fig. 4-11(a) is called peritectic (sometimes meritectic) because the solid S_2 here undergoes partial fusion, or melts to a liquid and a second solid. The same term is used whether the solid is a solid solution or (later) a definite compound.

The 4-phase invariant tie-line (two solids, liquid, vapor) is in every case the meeting of four 3-phase univariant equilibria, each of which is an isobaric, isothermal surface, appearing as a curved line in P/T projection, generated by 3-phase tie-lines: the S_1LV equilibrium (freezing point for S_1 or solubility of A in liquid B), which originates at O_A ; the S_2LV , from O_B ; the S_1S_2L , approaching the melting point region with falling P from the upper consolute point 4; and the S_1S_2V equilibrium from lower T and P . The approach of the first two univariant equilibria to the quadruple point may be from either higher or lower P , whatever their approach in regard to T .

If the MG is considered open, or if the critical curve of the MG is outside the limits of P and T in which the system is studied, then the space model may be said to contain two separate solid phases, each with its own space or volume. The S_1 space, for example, is now contained between four surfaces, being open at high P and low T : (1) the plane face defined by the SL and SV

curves of pure A; (2) an inner curved face which is the S_1 surface of the MG ; and two curved surfaces joining these two faces, namely (3) the solidus of the S/L equilibrium loop originating on the SL curve of A, and (4) the solidus of the S/V loop originating on the SV curve of A. The intersections of the three binary surfaces give the S_1 curves of the three univariant equilibria involving S_1 : surfaces 2 and 3 for the S_1S_2L ; surfaces 2 and 4 for the S_1S_2V ; and surfaces 3 and 4 for the S_1LV , from O_A to the quadruple point.

The lower extremity of the L/V loop is now no longer a continuous curve from O_A to O_B , but is interrupted by a break caused by the peritectic or eutectic 4-phase tie-line, the portion $l-v$ of this invariant tie-line being part of the L/V loop. In the eutectic case, therefore, the L/V loop begins to be cut with falling T , first at O_A and then at O_B , to end in the form of the flattened tip of a tongue, between points l and v of the eutectic tie-line (Fig. 4-11(c)).

The "condensed diagram" now represents only those equilibria projected in Fig. 4-11 which involve the vapor but without plotting the vapor composition (Fig. 4-12). The system $\text{AgNO}_3\text{--NaNO}_3$ is an example of the peritectic melting point relations of Fig. 4-12(a),⁸ while the eutectic case (Fig. 4-12(c)) is illustrated by $\text{KNO}_3\text{--TiNO}_3$ ⁹ and Cd--Pb .¹⁰

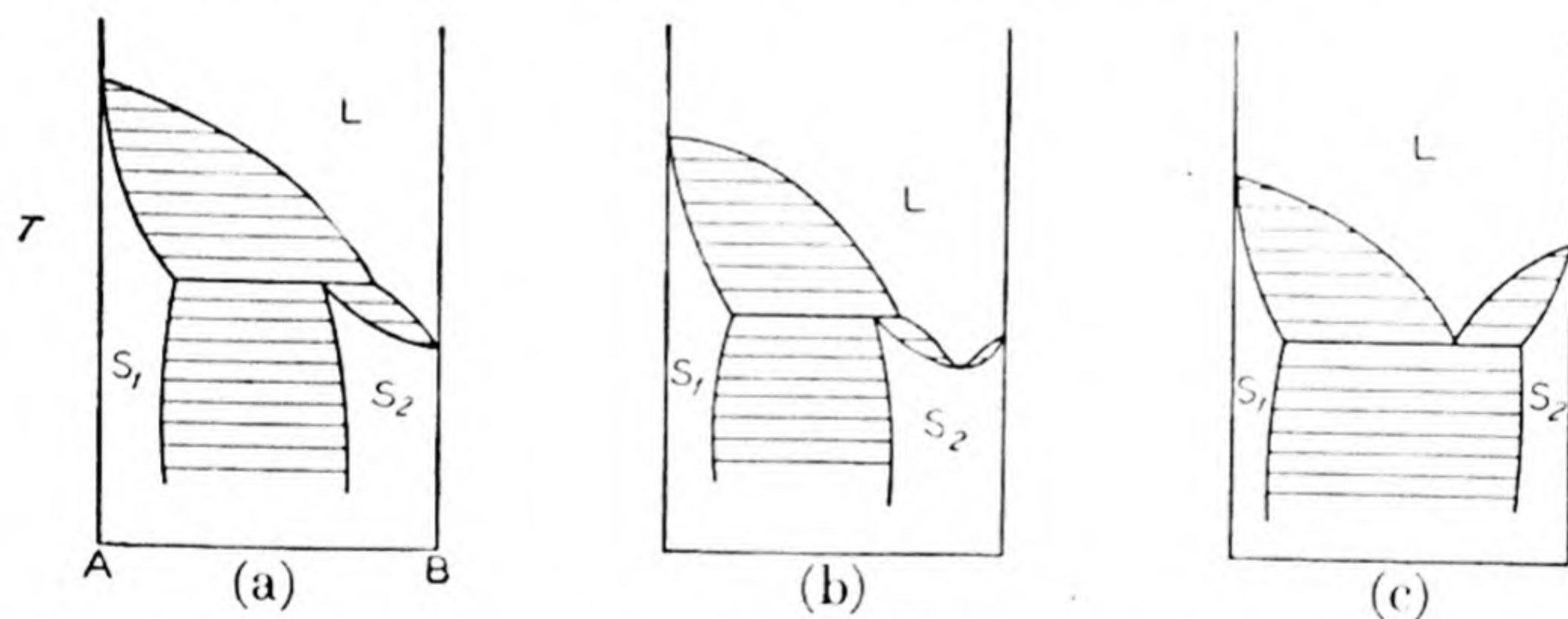


FIG. 4-12. Condensed diagrams for the systems of Fig. 4-11.

In P/T projection, Figs. 4-11(a) and 4-11(c) correspond respectively to Figs. 4-13(a) and 4-13(b). The P/T projection of a binary system shows fixed points (invariant or singular) and univariant curves (actual or by restriction). These include first of all the P/T diagrams of the separate components, with their triple and critical points. These unary points are joined by a system of binary curves, univariant 3-phase curves originating at unary triple points and the critical curve K_AK_B which, as we shall see later, may or may not be interrupted by a 3-phase curve. The 3-phase univariant curves either intersect, four at a time, at a binary quadruple point,

⁸ D. J. Hissink, *Z. phys. Chem.*, **32**, 542 (1900).

⁹ C. Van Eyk, *ibid.*, **30**, 430 (1899).

¹⁰ *I. C. T.*, vol. II, 411.

or end at an intersection with a binary 2-phase critical curve, that is, at a singular point type k , such as one of the critical solution points just discussed. The curves of restricted univariance, or identity curves, are either critical in nature (KK' and $K_A K_B$) or those (Chapter VII) for the congruent melting or sublimation of binary compounds; "azeotropic" curves, for maxima or minima of 2-phase transition loops, such as m_l and m_v of Fig. 3-13, are also univariant by restriction but are usually not shown.

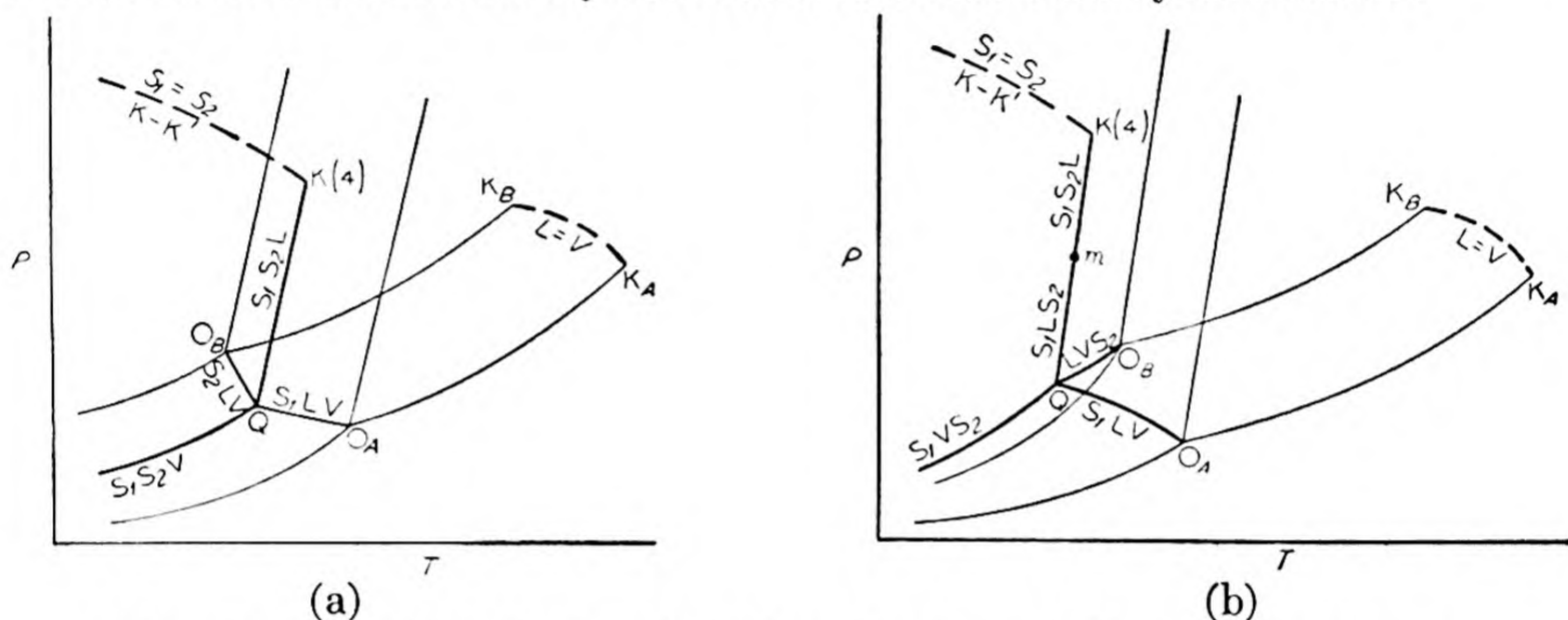


FIG. 4-13. P/T projections for (a) peritectic and (b) eutectic systems.

Univariant binary curves involving vapor and two solids or vapor and two liquids have positive P/T slope; all other binary curves may have any slope. At singular points, such as $K(4)$ of Fig. 4-13, the two curves may meet in any fashion, even both from higher T and higher P , etc. But at a quadruple point Q there must be at least one curve on each side of P_Q (that is, in respect to P) and at least one on each side of T_Q (in respect to T); the angle between two adjacent curves cannot be greater than 180° , and if there is only one curve on one side of T_Q or of P_Q it is the 3-phase system involving the two phases of extreme composition. These simple rules are part of the following general rule^{11,12} concerning the disposition of the four curves at a quadruple point. If the four phases are numbered 1, 2, 3, 4 in the order of their composition, and if the univariant system not containing phase 1 is called I, etc., and if the metastable extension of system I is called I' , then the order around the point Q , on the P/T projection, must be $I-II'-III-IV'-I'-II-III'-IV$. The rule can be useful in checking the correctness of the P/T data of the equilibria meeting at such a point, and in predicting the general position of one of the curves from the other three.¹³

¹¹ F. E. C. Scheffer, *Z. phys. Chem.*, **84**, 707 (1913).

¹² F. A. H. Schreinemakers, *ibid.*, **82**, 59 (1913).

¹³ For a later derivation of the rule, see G. W. Morey and E. D. Williamson, *J. Am. Chem. Soc.*, **40**, 59 (1918). These authors derive it as a special case of a general rule for the P/T relations of the univariant equilibria intersecting at an invariant point of a system of any order.

Chapter V Complete Immiscibility in the Solid State

A. The Solubility Curves

If the solid phases are pure A and pure B, the solid phase volumes of the space model, discussed in the preceding chapter, may be considered constricted to the terminal planes bounded by the SL and SV curves of each component, so that all tie-lines involving a solid phase must extend to the side of the diagram. The system is furthermore now always of the eutectic type since, with pure solids in equilibrium with liquid, the melting point is always lowered both from O_A and from O_B . Otherwise the general relations remain the same as long as the components are completely miscible in the liquid state, or as long, at least, as a liquid MG does not touch the S/L

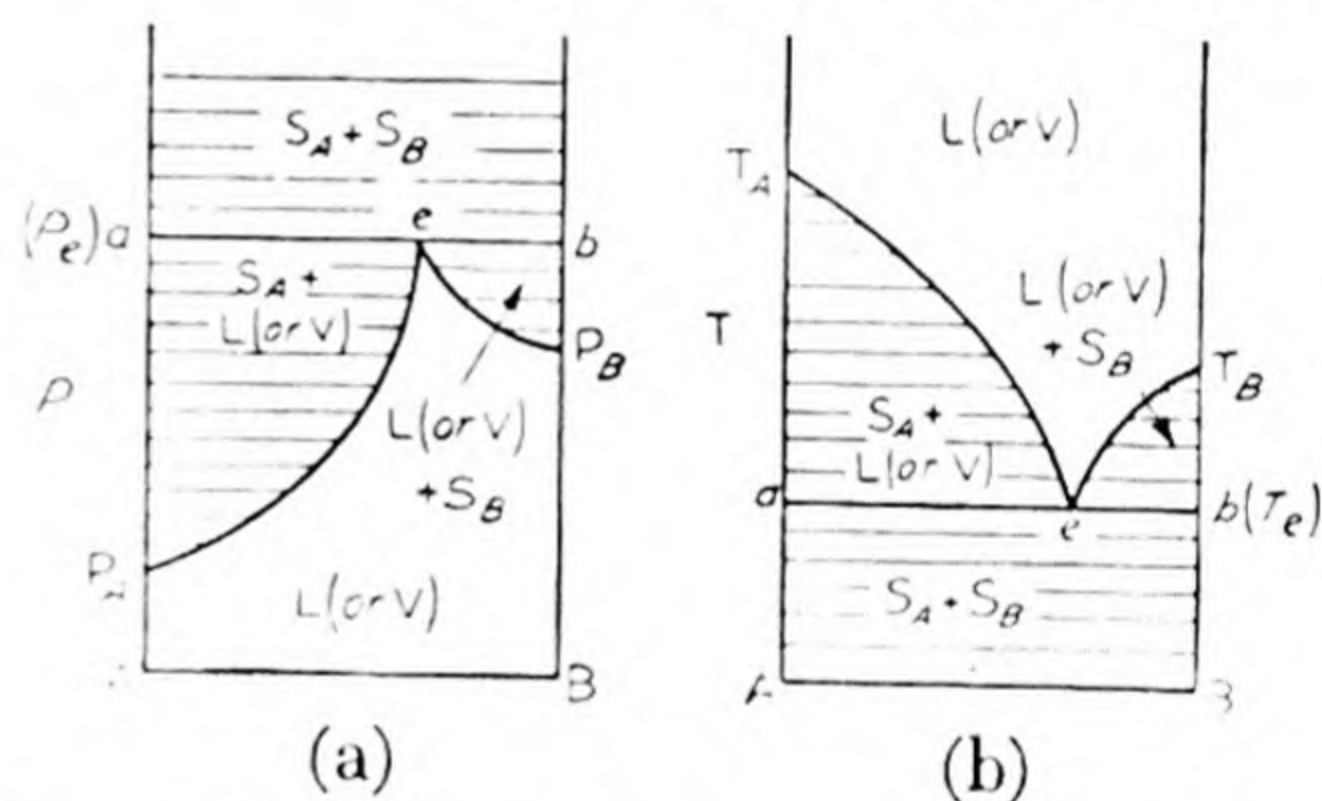


FIG. 5-1. Transition curves for complete immiscibility of solids.

transition loop; we shall, in fact, assume for our principal case that the L/V loop is of the ascendant type at the eutectic region. The chief modification, then, which will affect the "melting point relations," will be in the solid-vapor and solid-liquid equilibria, shown in Fig. 5-1 in isothermal and isobaric cross-sections; this is the case of Fig. 4-8(b) for zero miscibility. The simple relations of Fig. 5-1(b) are illustrated by the systems KCl-H₂O and Au-Tl;¹ Fig. 5-1(a), however, assuming the solid phase to be denser than the liquid, does not apply to the special case of aqueous systems, considered in Chapter VI, section E.

Again P_A is the vapor pressure or the melting pressure of pure S_A at the T of the section, and T_A the melting temperature or the sublimation temperature of pure S_A at the P of the section. P_e is the vapor pressure of the 3-phase equilibrium $S_A S_B V$ (ideally the sum of P_A and P_B , the vapor e containing the components in the molecular proportion $A/B = P_A/P_B = eb/ea$), or the pressure of the equilibrium $S_A S_B L (L = e)$. In Fig. 5-1(b), T_e is the

¹ M. Hansen, *Der Aufbau der Zweistofflegierungen*. Berlin, 1936; p. 265.

sublimation T of a mixture of S_A and S_B in equilibrium with vapor e , or the lowest freezing point of binary liquids at the specified P , the liquid e solidifying to a mixture of S_A and S_B in the proportions eb/ea .

The curves P_Ae , eP_B , T_Ae , and eT_B are transition curves or solubility curves. If Ph 2, the upper phase in respect to temperature, that is, L or V, is considered an ideal solution, these curves may be calculated from the SL or SV curves of the individual components. Since the SV curve of A involves the heat of sublimation, then T_Ae , the solubility curve of S_A in the binary vapor containing B, at constant total P , may be calculated from T_A , its sublimation T , and the heat of sublimation of A as $f(T)$, that is, from its SV curve and the molal volumes in the two states. The solubility of S_A in binary liquid, or the (ideal) effect of B on the melting point of A, at specified P , may similarly be calculated from T_A , its melting point, and its heat of fusion, either assumed as independent of T as a first approximation or as $f(T)$ from the fusion curve of A and the molal volumes in the two states.

If the composition is plotted in mole fraction, the melting point curve of each component, T_Ae or eT_B , is independent of the nature of the other component, ideally, and the intersection of the two curves gives the temperature and composition of the liquid e in equilibrium with both solids. Since the solubility of A at specified T and for a given value of the heat of fusion will fall (that is, move to the right in the diagram of Fig. 5-1(b)) as its melting point increases, the point e will move towards T_B as T_A rises; just as the vapor e , in Fig. 5-1(a), moves towards P_B as the volatility of A or P_A falls. In some cases the difference between e and T_B of Fig. 5-1(b) may be experimentally not detectable, as in the systems Si-Sn² and Ag-Na,³ and such systems are sometimes called "monotectic," although every binary system in which the solid phases are the pure components must be of the eutectic type if the substances are miscible as liquids.

If an impurity B, accompanying the substance A, is soluble in liquid A, it will affect the melting point of A in some way (except for the most extraordinary case mentioned in Chapter I in which two optical isomers, *d*- and *l*-camphoroximes, act as a single component, forming continuous solid solution of constant melting point).

If B is then "liquid-soluble" but "solid-insoluble" in A, the solid phase being pure A on freezing, the melting point of A is lowered. If B is also solid-soluble, forming a solid solution with A, the melting point may be either lowered or raised, regardless of the relation between the melting points of A and B, as seen in Chapter III. But in either case, whether or not

² Hansen, *loc. cit.*, p. 1041.

³ *I. C. T.*, II-422.

B is solid-soluble, an impure sample of A will display a **melting range**. Repeated purification will therefore either raise or lower the melting point, but it will always sharpen it or decrease the melting range. In the case of a solid-soluble impurity, this will be evident from Fig. 3-3(b). The melting range of the solid solution is the vertical distance, a temperature range, between solidus and liquidus; if B is the impurity in A, in Fig. 3-3(b), the melting range of A is seen to become shorter and to rise in T , as A is purified, while if A is the impurity in B, the melting range of B is also shortened, but lowered, as B is purified.

If the impurity B is solid-insoluble (Fig. 5-1(b)) the situation seems at first sight to be otherwise. Every mixture of A and B begins to melt, at equilibrium, at the eutectic temperature, T_e , and the range of melting is strictly longer the smaller the percentage of B on the A side of the eutectic liquid. But in practice the liquid, always first formed at T_e , will be more and more difficult to detect, the purer the sample of A, because the proportion of liquid formed varies in an inverse fashion with the B content of the sample. The sample will *appear* to start melting always at some temperature above T_e , so that as A is purified, its apparent melting range becomes shorter, and higher in temperature, until, as a limit for pure A, both the actual and the apparent melting ranges vanish to zero at the constant melting point, T_A .

If a sample has a perfectly sharp melting point (no range, no dependence on ratio of melting), it is not necessarily a single, pure component, unless the melting point also remains sharp through changes of P , whereby it will be distinguished from a eutectic mixture and from a solid solution of minimum freezing point (but not from a racemic sample of optical isomers).

If B is water and A a salt or other solid, eT_B is the "ice curve" and T_Ae the solubility curve of the solid A, at the P of the diagram. The slope of the ice curve is always found to be positive (the heat of solution always positive); but the slope of any solubility curve in general may change its sign over part of its course. Various cases such as those shown in Fig. 5-2 are possible. Unsaturated solutions lying below the curve $m'm$ (Fig. 5-2(a)⁴) or em (Fig. 5-2(b)) will precipitate A when heated to the solubility curve, and then of course redissolve the solid on again crossing the solubility curve above m into the area of homogeneous liquid. The system $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ illustrates a eutectic of the type of Fig. 5-2(b).⁵

⁴ For at least the theoretical possibility of such a diagram, see Roozeboom (Ref. P), vol. II, part 1, p. 313; also H. W. B. Roozeboom and A. H. W. Aten, *Z. phys. Chem.*, **53**, 419, 1905, in connection with pseudobinary and pseudoternary systems.

⁵ A. N. Campbell, *J. Am. Chem. Soc.*, **65**, 2268 (1943).

The general course of the solubility curve, T_Ae , is given by the fundamental relation of the isochore,

$$\frac{dx_A}{dT} = \frac{x_A L_A}{RT^2}, \quad (1)$$

in which x_A is the mole fraction in the liquid of the saturating solid component A, and L_A is its heat of solution. The solubility therefore normally increases with T , but if L_A becomes negative through a particular temperature range, the solubility falls with increasing T in that range. Hence curves like those of Fig. 5-2(a) and 5-2(b) indicate a change of sign of L_A with temperature. Furthermore,

$$\frac{d^2x_A}{dT^2} = \frac{x_A}{RT^2} \left[\frac{L_A}{RT} \left(\frac{L_A}{T} - 2R \right) + \frac{dL_A}{dT} \right]. \quad (2)$$

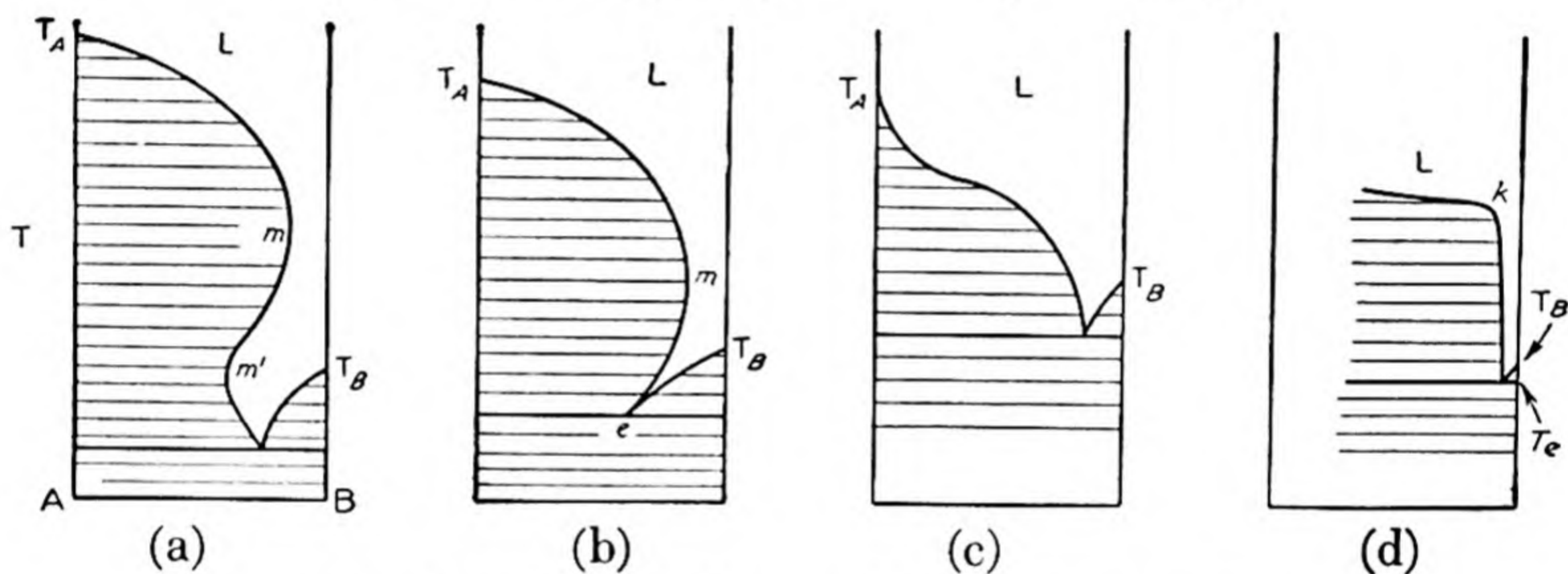


FIG. 5-2. Other shapes of solubility curves.

The curvature of T_Ae therefore depends on the value of L_A relative to the temperature, or on the value of the entropy of solution, L_A/T , and also on the sign and magnitude of dL_A/dT .

In the ideal case L_A is taken as the heat of fusion ΔH_A , and is assumed moreover to be independent of T . Now if $\Delta H_A > 2RT_A$, therefore, with T_A the melting point of A, the curve is concave downward from the start, and it continues simply to become steeper as T falls and the eutectic is approached. If $\Delta H_A = 2RT_A$, the curve starts as a straight line and then becomes concave downward as T decreases. Finally if $\Delta H_A < 2RT_A$, the curve starts concave upward, as in Fig. 5-2(c), but then passes through a point of inflection when $T = \Delta H_A/2R$, $x_A = e^{-(2 - \Delta H_A/RT_A)}$, and $dx_A/dT = 4Rx_A/\Delta H_A$, after which it becomes concave downward to the end.

In the ideal case, then, or at any rate with L_A independent of T , the second derivative of the solubility with respect to T always decreases (algebraically) with increasing T . It may change from positive to negative but not in the other direction. Or, if the freezing point curve starts, at T_A , as in Fig. 5-1(b), the curvature never changes in sign, while if it starts as

in Fig. 5-2(c) it ultimately changes its curvature. The curve, however, may be interrupted before it undergoes its inflection by intersection with the curve for a different solid phase, such as component B at the eutectic, a lower temperature polymorphic form of A, or a compound.⁶

This effect of the magnitude of ΔH_A on the curvature of the freezing point or solubility curve in the ideal case cannot generally be very large. A pronounced change of curvature, such as that shown in Fig. 5-2(c) on the other hand, suggests a different explanation. Such "S-shaped" solubility curves will be discussed later in connection with the possibility of a miscibility gap in the liquid state (Chapter VIII). Some alloy systems with freezing point curves of the general appearance of Fig. 5-2(c) are Zn-Sn,⁷ Na-Rb⁸ and Ag-Na.⁹

Fig. 5-2(d) shows the case of a solid the solubility of which is at first hardly affected by increasing T , starting from the eutectic, T_e , and then at a certain temperature shows a marked increase in slope (dc/dT). This behavior is characteristic of "colloidal electrolytes." The region near k , where this sudden change of slope occurs, near a characteristic temperature and characteristic concentration, is related to the Krafft point¹⁰ of the aqueous solution of such a substance. This region seems to involve a critical concentration, depending upon the temperature, marked by a break in the conductance curve which is explained through the formation of ionic micelles. Since each micelle still acts as a single particle, a much greater analytical concentration then becomes necessary in order to maintain saturation in accordance with the solubility product principle; in this way the great increase of solubility above the temperature k may presumably be explained.¹¹

B. The Space Model; Projections and Sections

Keeping the same relation of O_A to O_B as in Fig. 3-1, we shall first consider the simple case in which P_E , the pressure of the eutectic equilibrium, is intermediate between P_{O_A} and P_{O_B} , with no maximum or minimum of P in

⁶ For fuller discussion, see Roozeboom (Ref. P.), Vol. II, part 1, pp. 273-287; also A. W. Davidson, W. J. Arisinger and C. I. Michaelis, *J. Phys. Colloid Chem.*, **52**, 332 (1948).

⁷ C. T. Heycock and F. H. Neville, *J. Chem. Soc.*, **71**, 383 (1897).

⁸ Hansen, *loc. cit.*, 923.

⁹ *I. C. T.*, II, 422.

¹⁰ F. Krafft and H. Wiglow, *Ber. deutsch. chem. Ges.*, **28**, 2526 (1895).

¹¹ On the break in conductivity see, for example, A. W. Ralston, C. W. Hoerr and E. S. Hoffman, *J. Am. Chem. Soc.*, **64**, 97 (1942), and A. W. Ralston and C. W. Hoerr, *ibid.*, **64**, 772 (1942); on the solubility effect, A. W. Ralston and C. W. Hoerr, *ibid.*, **68**, 851 (1946). According to E. P. Martin and R. C. Pink, *J. Chem. Soc.* (1948), p. 1750, however, the effect cannot have this cause in the case of the solubility of zinc soaps in organic solvents. Moreover, a similar shape may be noted in the freezing point curves of silicon in the systems Si-Sb and Si-Sn; Hansen, *loc. cit.*, 1013, 1071.

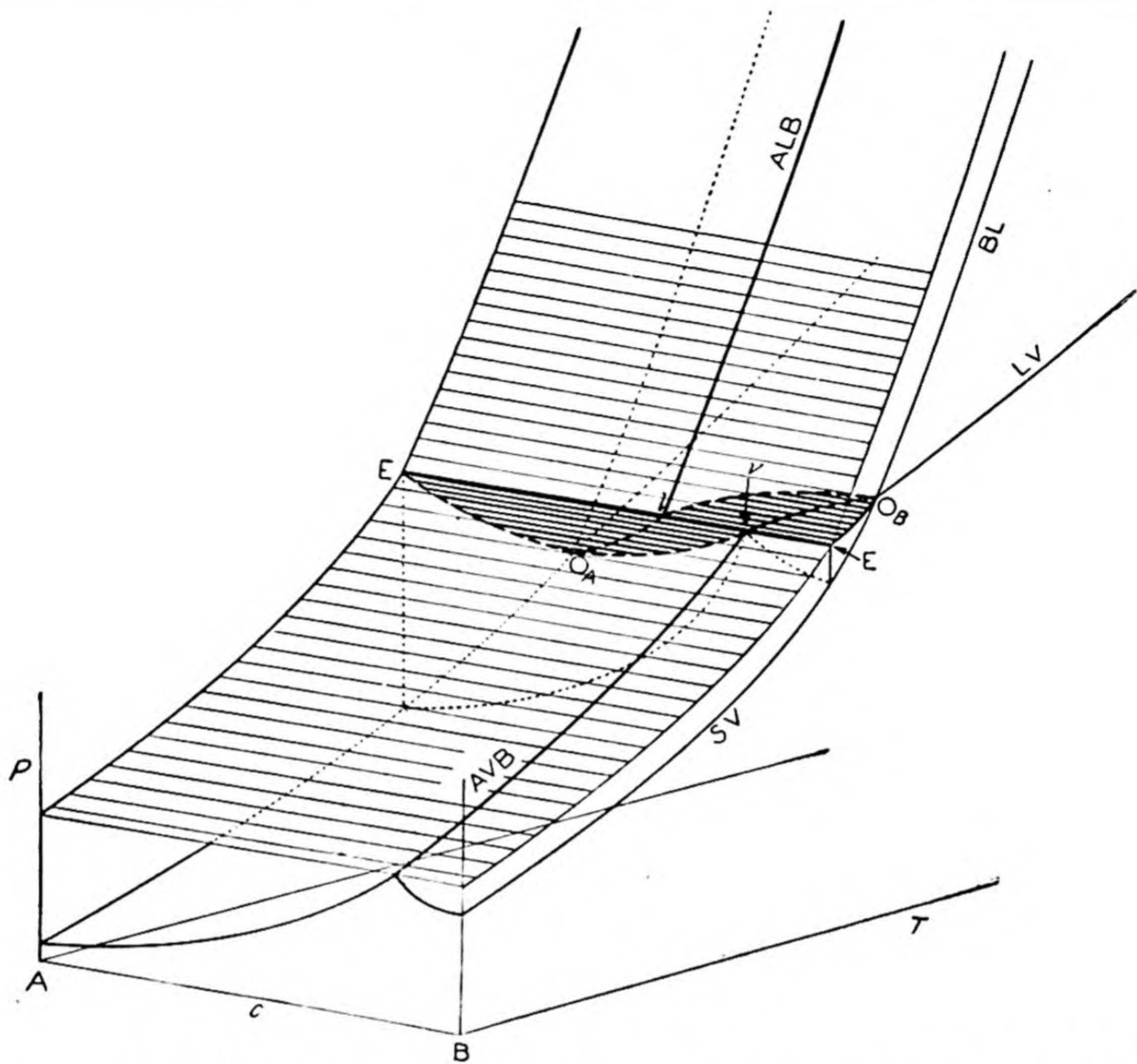


FIG. 5-3. The "melting region," with complete immiscibility of solids.

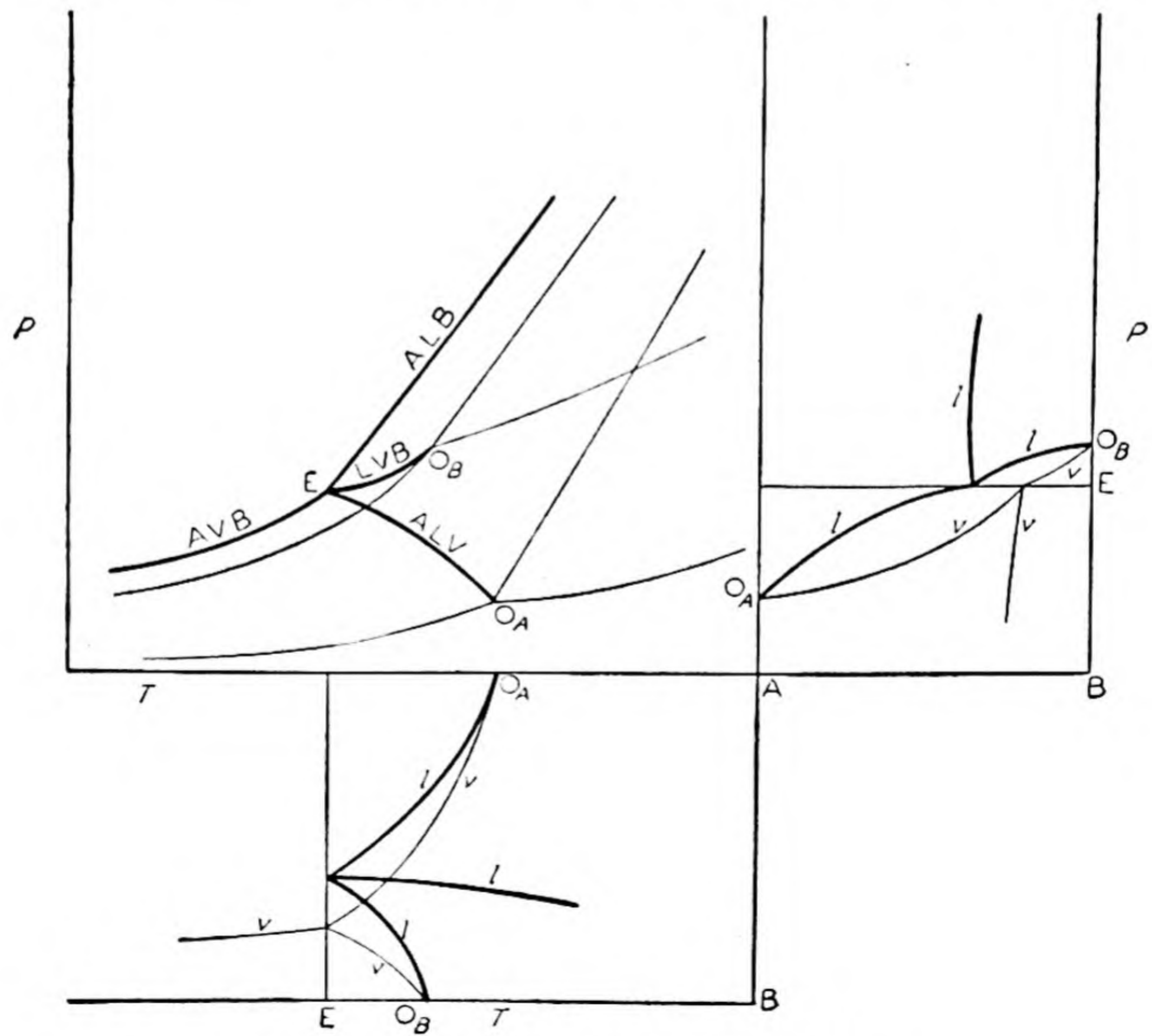


FIG. 5-4. Projections of Fig. 5-3.

either EO_A or EO_B ; we also assume the L/V loop to be simple, or "ascendant" in type. The 3-dimensional model is shown in Fig. 5-3, and its projections in Fig. 5-4.

Fig. 5-4 shows the four 3-phase equilibria, LVB¹² from O_B , ALV from O_A , AVB from low T and P , and ALB from high P , intersecting at the quadruple point E, which is the eutectic tie-line E/vE of Fig. 5-3, extending from pure A to pure B. Fig. 5-3 also shows the tie-lines of the four 3-phase equilibria just mentioned. The AVB system, extending across the model, is viewed from above, and through it is seen the system ALV originating at O_A and proceeding to the eutectic with rising P and falling T . The system ALB, viewed from the low P side, also extends across the model; through it is seen the system LVB originating at O_B and descending to the eutectic in respect to both P and T .

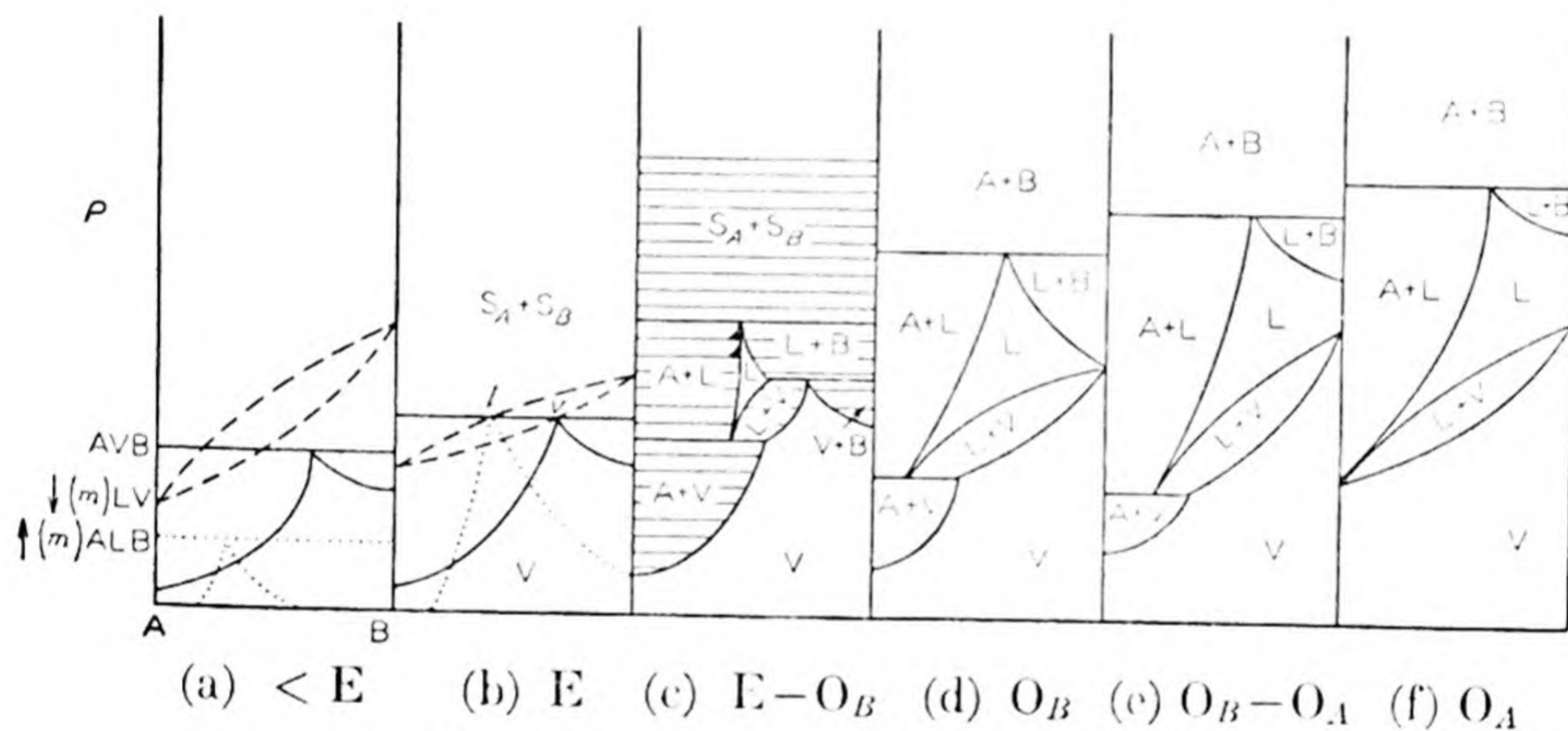


FIG. 5-5. Isotherms for Fig. 5-4.

Representative isotherms are shown in Fig. 5-5. The relation between Fig. 5-5(d) and Fig. 3-14(d) will be clear when it is remembered that if the solid components are immiscible all the tie-lines of the latter figure involving the solid phases would be extended to the sides of the diagram, whereupon the maximum m_i becomes the 3-phase tie-line $S_A L S_B$ of Fig. 5-5(d). Fig. 5-6 shows the representative isobars; the principle is again that of the order in which the three classes of equilibria, SL, SV, and LV, are cut by isobars and isotherms on the two sides of the melting region, as explained in Chapter III. If the pressure of E is lower than both O_A and O_B (with no pressure maximum in either of the solubility curves EO_A and EO_B) then the $(T/c)_P$

¹² The phases involved in 3- and 1-phase equilibria will always be given in the order of increasing B content. This will help in verifying the configuration of the four curves at an invariant point, according to the rule stated at the close of the previous chapter. The order also becomes important in itself in connection with relations of binary compounds, to be discussed in Chapter VII.

sections will appear, schematically, just like the $(P/c)_T$ sections turned upside down. [Note: In this and in other similar sets of juxtaposed sections, the relative value of the ordinate has frequently been changed arbitrarily from one section to the next for economy of space. Fig. 5-6(e), for example, must be imagined as representing temperatures higher than those of corresponding points in Fig. 5-6(d).]

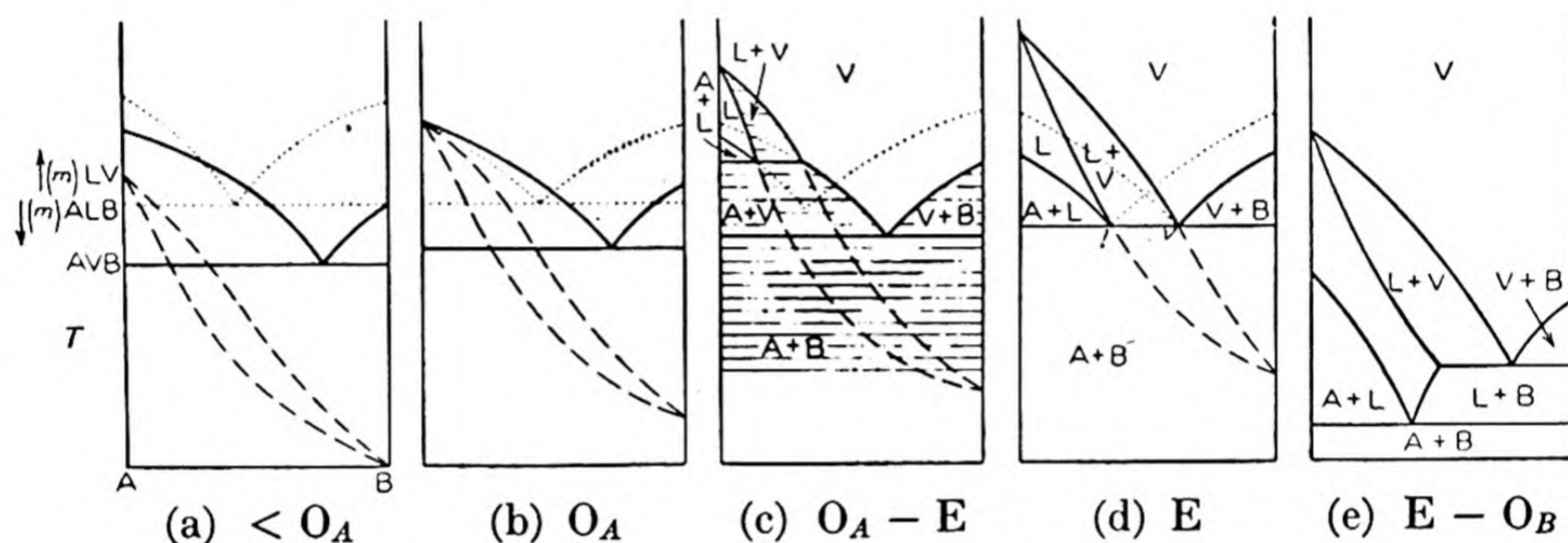
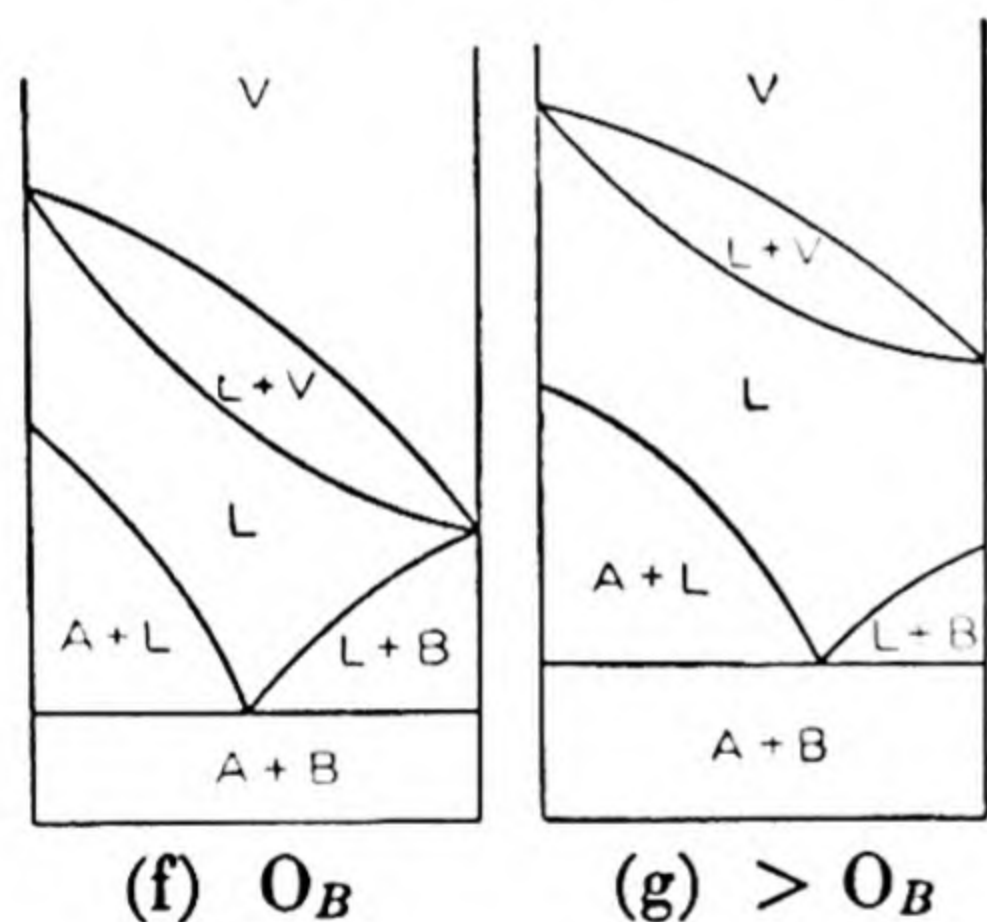


FIG. 5-6. Isobars for Fig. 5-4.



The diagrams of Figs. 5-3 to 5-6 assume the simple case of an ascendant L/V loop. If this loop has a $P_{min.}$ and $T_{max.}$ on the A side, we may imagine the $P_{min.}$ to cross the 3-phase tie-line ALV of Fig. 5-5(c) at a temperature (T_x) just above that of the figure, at a singular point of type m , above which the isotherm would have the appearance of Fig. 5-7. The T/c projection would be

Fig. 5-8, which is to be compared with that of Fig. 5-4. The point x is seen to mark a reversal in the order of the three phases for the equilibrium running from O_A to the eutectic; below T_x , the order is as in Fig. 5-5(c), ALV , and above T_x , AVL . If the L/V loop has a $P_{max.}$ and $T_{min.}$,¹³ on the B side, the $P_{max.}$ crosses the 3-phase tie-line LVB of Fig. 5-5(c) at a singular point, T_y , just above the temperature of Fig. 5-5(c), giving the isotherm of Fig. 5-9. In the T/c projection of Fig. 5-10 the point y again marks a change in the order of phases, from LVB between the eutectic and y , to VLB from y to O_B .

The solubility curves EO_A and EO_B cannot have maxima or minima of T , but they may show considerable variety in P . P_E must be above the sublimation curves of the components, but it cannot be greater than the sum

¹³ For fuller discussion, see E. Jänecke, *Z. phys. Chem.*, A-182, 177 (1938).

of the separate sublimation pressures at T_E . It may otherwise have any relation to O_A and O_B , above, between, or below the two. Furthermore the solubility curve EO_A of the higher melting component frequently passes through a maximum in P ; ¹⁴ theoretically either or both solubility curves

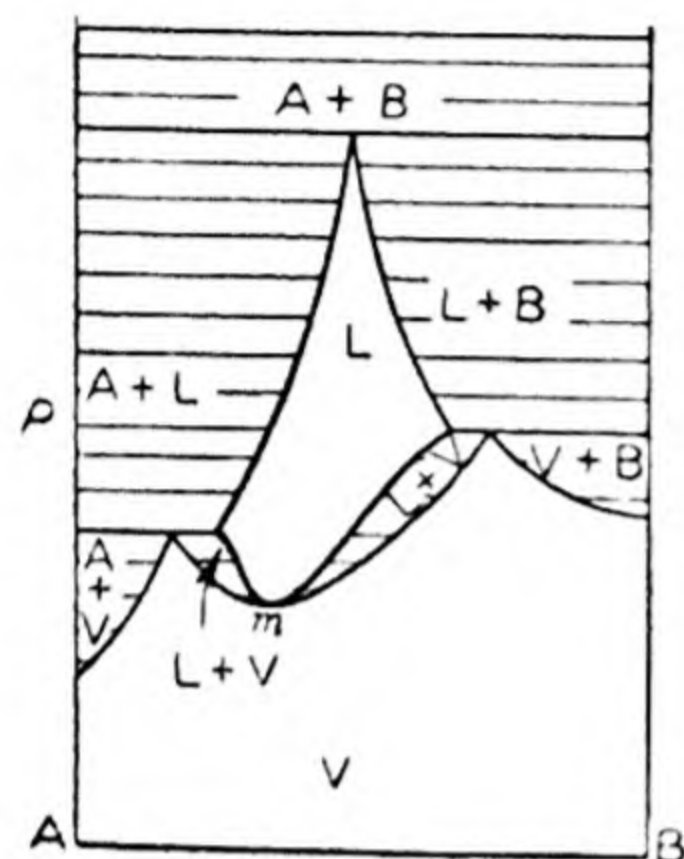


FIG. 5-7. Variation of Fig. 5-5(c), with azeotropic L/V relation, $P_{min.}$

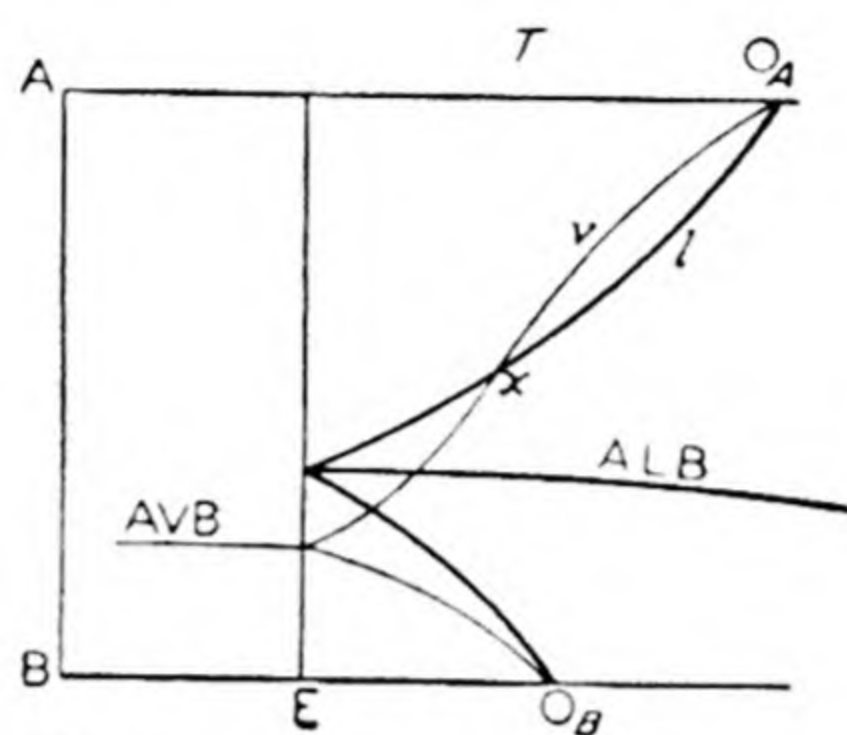


FIG. 5-8. Variation of Fig. 5-4, with azeotropic L/V relation.

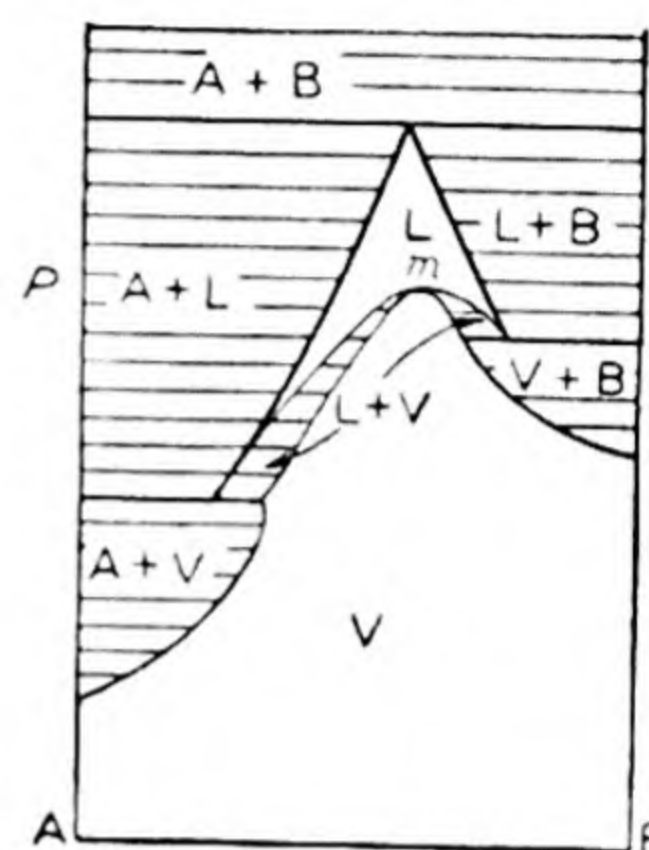


FIG. 5-9. Variation of Fig. 5-5(c), with $P_{max.}$ in L/V relation.

may behave in this way. If there is a $P_{max.}$ (P_m) in EO_A , as in Fig. 5-11, the isotherms of the system are still of the form of Fig. 5-5, but the isobars will appear as in Fig. 5-12, for some representative pressures.

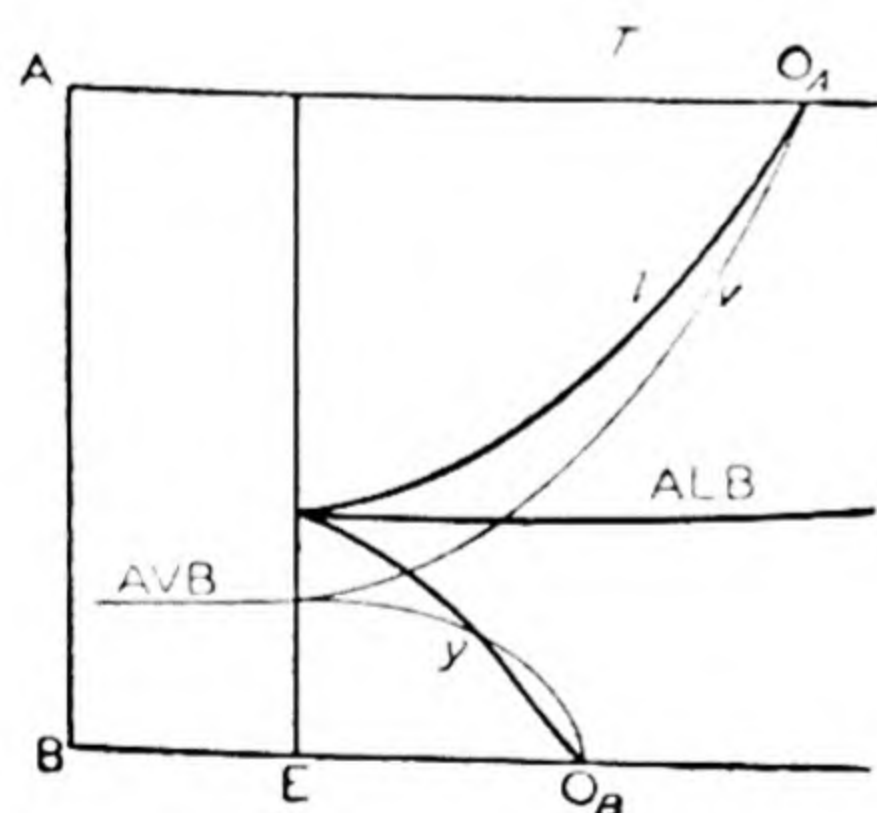


FIG. 5-10. Another variation of Fig. 5-4, with azeotropic L/V relation.

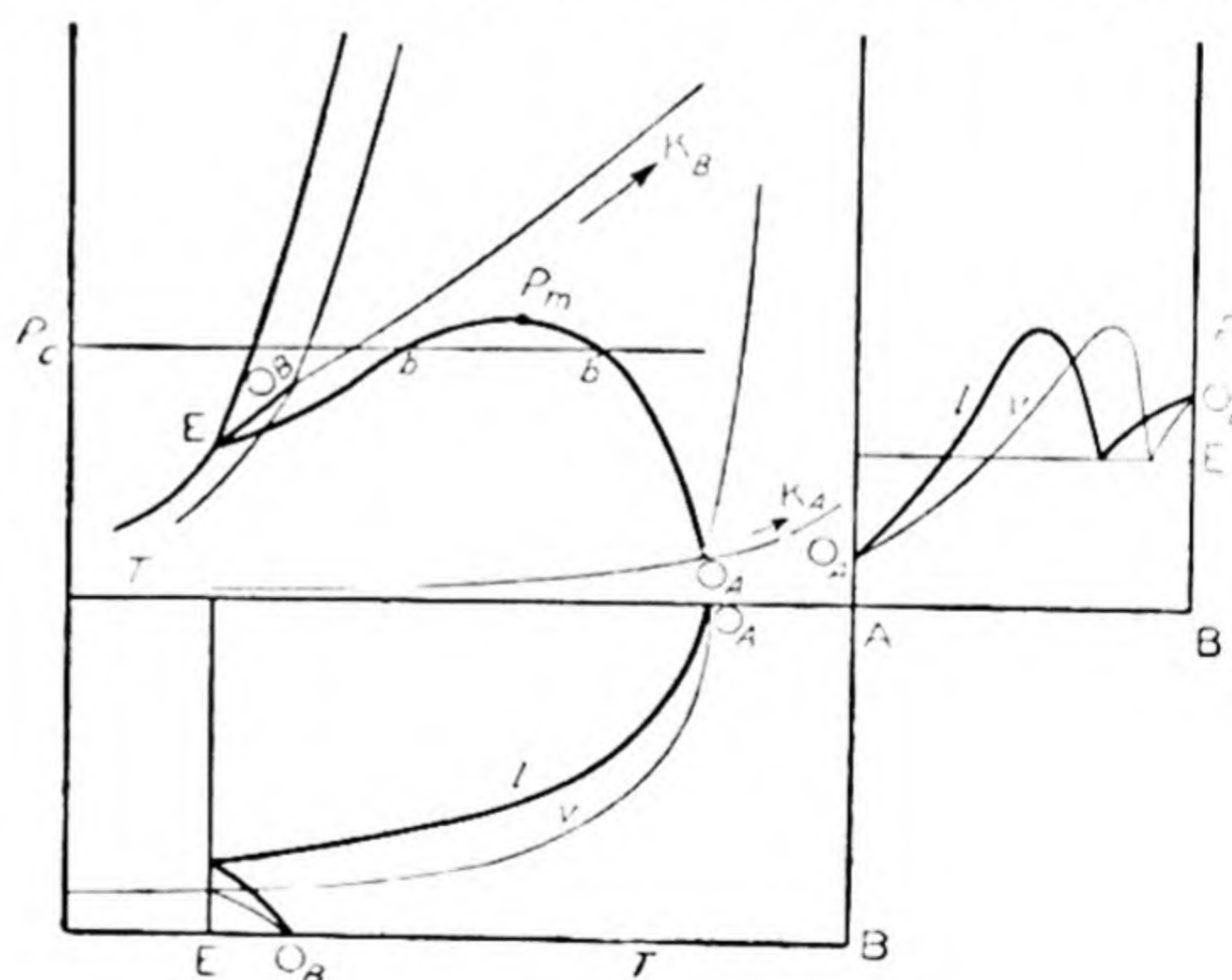


FIG. 5-11. $P_{max.}$ in the equilibrium ALV, curve EO_A .

In Fig. 5-3 the curved line lO_B is the lower limit of a curved surface joining the liquid of the "eutectic curve" ALB and the fusion curve BL of pure B. This is the "solubility surface" of solid B; it is generated by the

¹⁴ For some examples, in systems of water and salts such as alkali halides, see N. B. Keevil, *J. Am. Chem. Soc.*, **64**, 841 (1942). For the calculation of the temperature of P_m from the melting point of the salt, in (ideal) aqueous salt systems, see A. E. Korvezee and P. Dingemans, *Rec. trav. chim. Pays-Bas*, **62**, 653 (1913).

solubility curve or the liquid of the equilibrium of liquid + solid B of the various sections of Figs. 5-5 and 5-6. A similar solubility surface of A joins the "eutectic liquid" with the fusion curve of A, the surface ending at the line lO_A of Fig. 5-3, its intersection with the L/V loop. The relation of T , P , and x_B on the solubility surface of B is given by Braun's law,

$$\left(\frac{\partial x}{\partial P}\right)_T \left(\frac{\partial x}{\partial T}\right)_P = -T \Delta V/L, \quad (3)$$

in which ΔV is the change in volume per mole of solute added to an infinite quantity of the saturated solution, and L is the change in heat content accompanying the process.¹⁵ An equation may also be written for the ideal

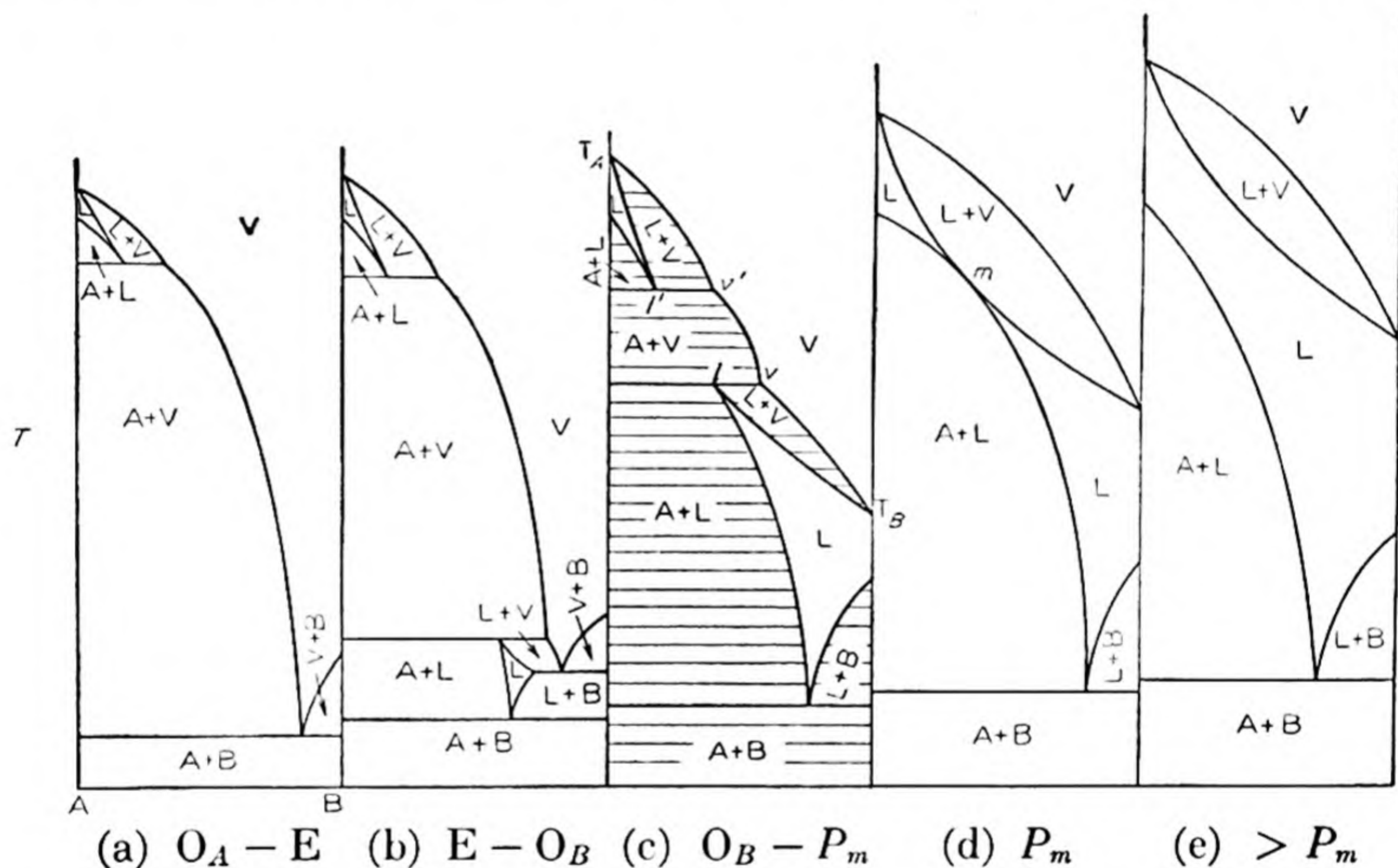


FIG. 5-12. Isobars of Fig. 5-11.

relation between the composition and the temperature T_e , or the pressure P_e , on the eutectic curve itself:¹⁶

$$\frac{T_B - T_e}{T_B} \bigg/ \frac{T_A - T_e}{T_A} = \frac{x_A}{x_B}, \quad (4)$$

$$\frac{P_B - P_e}{P_B} \bigg/ \frac{P_A - P_e}{P_A} = \frac{x_A}{x_B}, \quad (5)$$

¹⁵ F. Braun, *Annalen der Physik*, [3], **30**, 250 (1887); E. Cohen, K. Inouye and C. Euwen, *Z. phys. Chem.*, **75**, 257 (1910); E. Cohen and A. L. T. Moesveld, *ibid.*, **93**, 385 (1919).

¹⁶ E. Kordes, *Z. anorg. Chem.*, **154**, 93 (1926); **167**, 97 (1927); *Z. phys. Chem.*, **152**, 161 (1931); see also the discussion in Roozeboom (Ref. P), Vol. II, part 1, pp. 411-432, and H. A. C. McKay and B. Higman, *Phil. Mag.* (London, Edinburgh and Dublin), [7], **19**, 367 (1935).

in which T_A , T_B , P_A , P_B are the melting temperatures and pressures of the individual components.

For systems of low vapor pressure, such as aqueous salt systems, the normal condensed eutectic or that observed in open air is practically identical with the true invariant point, both in temperature and in the composition of the liquid phase. The constancy of the composition of this eutectic salt solution led originally to the view that it represented a definite compound of the components. The solid mixture of salt and water produced by solidification of the liquid, and having its constant composition, came temporarily to be called a *cryohydrate*, and an ice-salt eutectic is still sometimes called a *cryohydric point*. The "constant boiling" liquid of azeotropic systems similarly appeared at first to be a definite compound, but there, too, variation in pressure causes a change both in the temperature and in the composition of the "constant boiling" liquid.

Finally, the SL curves of both components have been assumed to have positive P/T slopes in Figs. 5-3 to 5-6. If the two fusion curves have negative slopes, the relations are still symmetrical and easily conceived, but the case would have no general importance. When one slope is negative and the other positive, as with practically any known aqueous system, the relations are rather special at the melting region. In either case, however, the slopes finally become positive at high P , as a result of high pressure polymorphism. Hence the special case of an aqueous system will be considered under polymorphism, in the next chapter, section E-3.

C. Boiling of Saturated Solutions

The isobar of Fig. 5-12(c) corresponds to that of Fig. 5-6(g) in that its pressure is above both O_A and O_B . In Fig. 5-6(g) the only vapor equilibrium is one of unsaturated liquid ("unsaturated" meaning here, as it conventionally does, not saturated with solid); if then the pressure of the isobar is that of the atmosphere, this means that only unsaturated solutions reach the boiling point, and the behavior of the binary liquids during boiling is described by the relations already discussed in Chapter III. In Fig. 5-12(c), on the other hand, the vapor equilibrium is divided into several parts. The L/V loop itself is in two sections, one for unsaturated liquids from the boiling point of B, T_B , to the liquid l , and one for unsaturated liquids from liquid l' to T_A , the boiling point of A. The two equilibria, Alv at lower T and $Al'v'$ at higher T , are isobarically invariant; the temperatures are given by the intersections, b and b' , respectively, of the solubility curve EO_A with the isobaric line P_c , on Fig. 5-11. For the system $\text{AgNO}_3\text{-H}_2\text{O}$, with $P_c = 1$ atm, the temperature of point b is 132.7° (normal boiling point of saturated solution), that of point b' is 191.0° , and the maximum, P_m , occurs at 1000

mm pressure and 168.5° ; the solid phase, however, is not the same at b and b' , since AgNO_3 undergoes an enantiotropic transition at 159.9° .¹⁷ Liquids boiling on the curve $T_B l$, for example, begin to precipitate S_A on reaching the composition l , where the liquid then boils at constant T , as a saturated liquid. If the system is a closed one, this point is not reached unless the total composition is on the left of point v , for if the concentration of A in the system is smaller than that at v , the liquid is entirely vaporized before it can become saturated with A; but if the composition of the liquid to be boiled (in the closed system) lies between l and v the tie-line Alv is reached, and as boiling proceeds the temperature and the compositions of the phases remain constant until the liquid is all consumed, leaving the 2-phase, isobarically univariant equilibrium of $A + V$. Continued heating at constant pressure causes disappearance of the solid on curve vv' if the composition lies between v and v' . Otherwise the next 3-phase tie-line, $Al'v'$, will be reached, which is, so to speak, an isobarically invariant *inverse* boiling point (the implication may be misleading if this is called merely a "second" boiling point); liquid reappears, of composition l' , and the temperature remains constant until, if the composition lies between l' and v' , the solid phase is consumed, leaving again an unsaturated LV system described by the curves $T_A l'$ and $T_A v'$.

If a liquid below the curve $T_B l$ is boiled in the open, and the vapor is removed as it is formed, the liquid may be expected to reach point l and there boil at constant temperature, giving off the vapor v and depositing solid A, the process stopping only when pure S_A is left, which then behaves as a one-component system in the open.

If the pressure is greater than P_m , the maximum of the EO_A curve of Fig. 5-11, then the boiling behavior, whether in a closed system or in the open, will be entirely similar to that of the system shown in Fig. 5-4.

Fig. 5-13 shows a system in which O_A is higher than O_B in both T and P . The curves c_0, c_1, \dots, c_7 , from the LV curve of pure B to that of pure A, are the vapor pressures of unsaturated solutions of constant composition, the concentration of A in the liquid increasing from c_0 to c_7 . At P_1 the isobar is the usual one, as in Figs. 5-6(g) and 5-12(e), in which only unsaturated solutions boil. At P_2 the isobar is shown in Fig. 5-14. The behavior of any unsaturated liquid (limited to concentrations of A smaller than c_4 at this P), when heated isobarically in a closed system, will be evident from Fig. 5-14. But if such a binary liquid is heated in the open, and if it loses no appreciable quantity of vapor until the boiling point is reached (P_2 now being the atmospheric P), then it boils, depending upon the concentration,

¹⁷ P. Dingemans and K. van den Berg, *Rec. trav. chim. Pays-Bas*, **61**, 605 (1942).

at a temperature between T_0 and T_4 (Fig. 5-13). As the liquid boils it loses vapor and becomes richer in A, until the solubility curve of A is reached at the concentration c_4 and the temperature T_4 . Now the system is isobarically invariant and boils at constant temperature until the liquid is consumed, leaving $S_A(+v)$, as seen in Fig. 5-14.

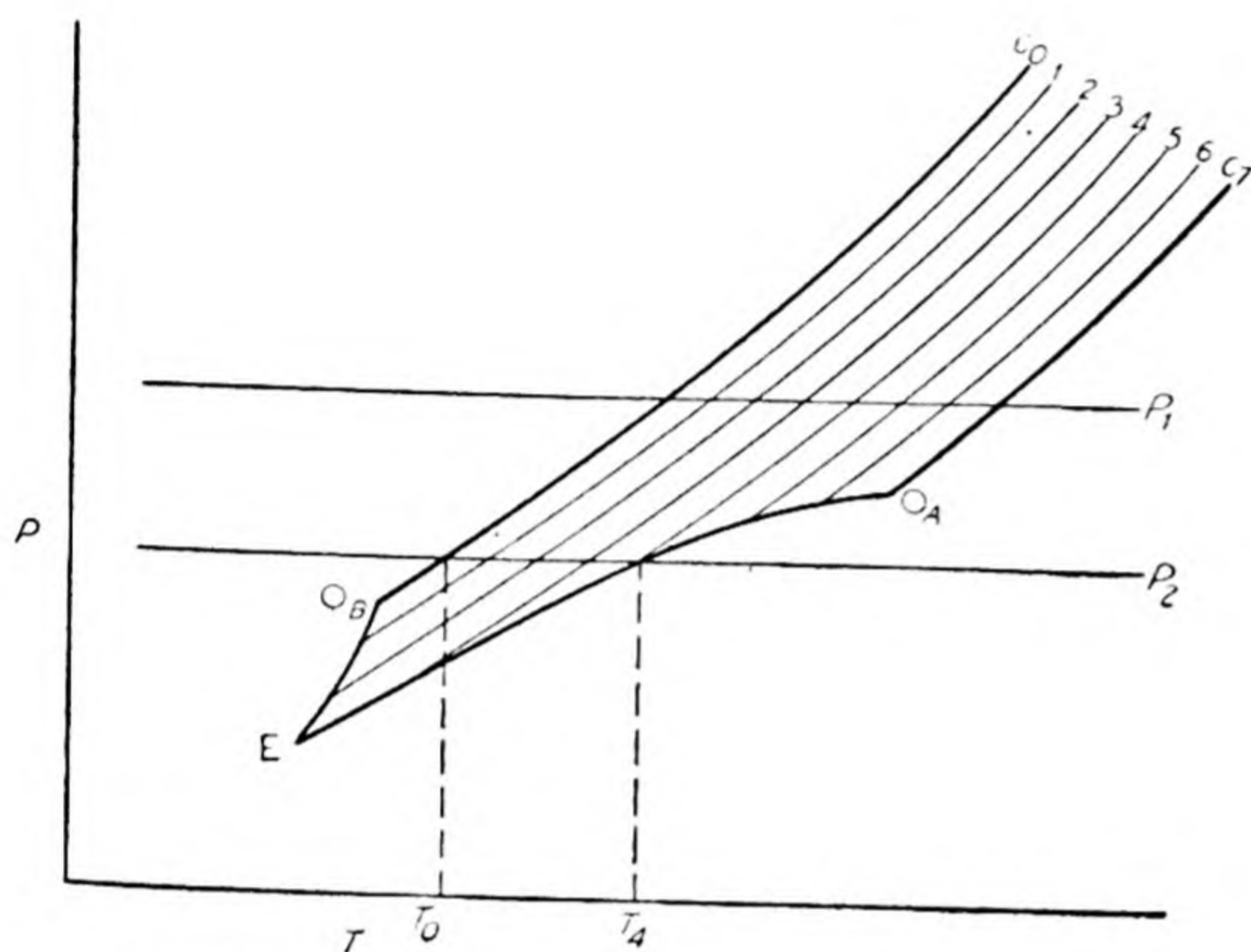


FIG. 5-13. P/T relations for solutions of various concentrations.

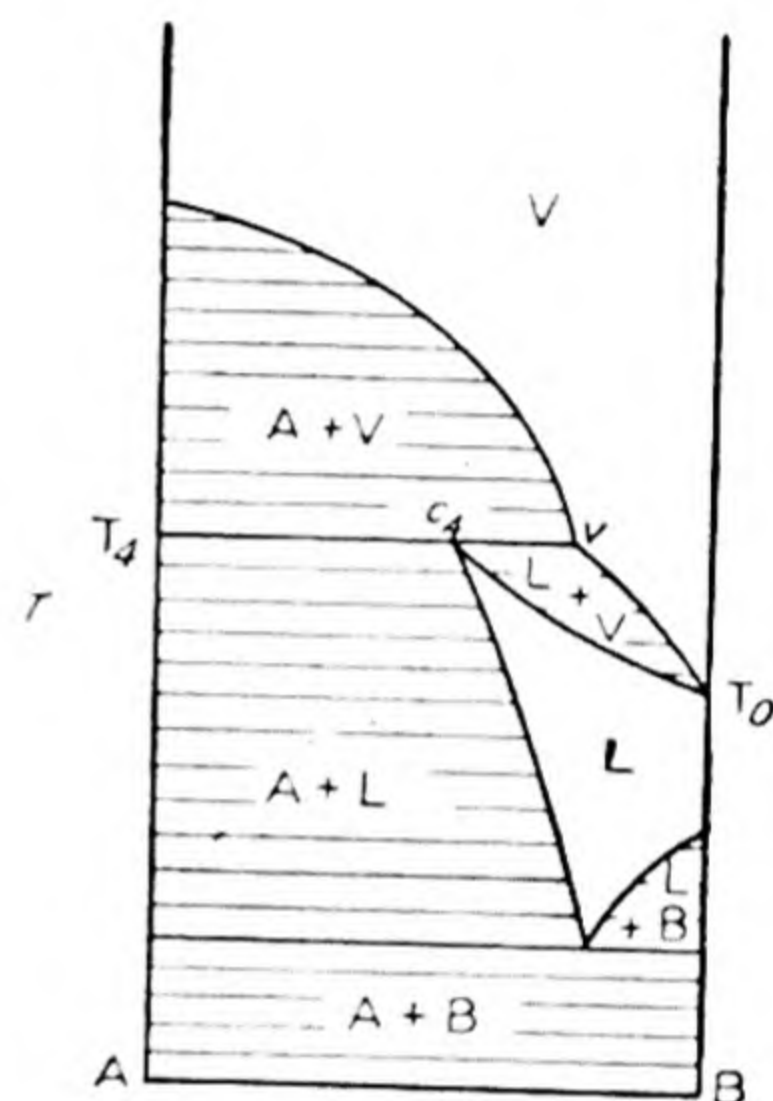


FIG. 5-14. An isobar of Fig. 5-13 at P_2 .

In any case (Figs. 5-4, 5-11, 5-13) solid A cannot be obtained by boiling its solution if the pressure is higher than the maximum of the solubility curve EO_A . Only if the solution is boiled at a pressure below this maximum, which may be O_A itself, as in Fig. 5-13 (but not E as in Fig. 5-4), or somewhere between E and O_A as in Fig. 5-11, can the solid be crystallized from the boiling solution.

As shown in Figs. 5-2(a) and 5-2(b), there may also be a minimum on the curve EO_A in respect to the concentration of A, or its solubility; Fig. 5-2(b) is now to be taken as the projection of the curves EO_A and EO_B , ignoring the vapor phase. The case of Fig. 5-2(b) is shown in Fig. 5-15, which is to be compared with Fig. 5-11, in which the solubility of A was assumed to increase continuously with T , while still giving a pressure maximum on the curve EO_A . Now if the atmospheric P is P_1 (Fig. 5-15), liquids with $c_A < c_1$, with c_1 corresponding to c_m of Fig. 5-2(b), will reach the boiling point as unsaturated liquids, from any initial T , and remain unsaturated until completely vaporized. Liquids of higher A concentration will reach the boiling point (the isobar P_1) only if they originate outside and above the solubility curve $c_m O_A$. If they lie originally at temperatures on the left of Ec_m , they begin to precipitate A on reaching the solubility curve.

tectic, such as that of Fig. 4-13(a), the phase reaction is $S_1 + L(+V) - \text{cals.} \rightleftharpoons S_2(+V)$; at a eutectic, such as that of Fig. 5-4, the phase reaction is $A + B(+V) + \text{cals.} \rightleftharpoons L(+V)$. When the heat of the phase reaction is large and the temperature of the equilibrium is low, as in many salt-water binary eutectics, the mixture may be used as a "freezing mixture."

If ice and a soluble salt, which may or may not be hydrated, are mixed at room temperature, the temperature will drop as the binary liquid is formed, because of the endothermal processes of solution of the solids; and if the mixture is stirred, to approach and maintain a 4-phase equilibrium (vapor being present), the constant eutectic temperature will prevail as long as both solids are still present. The eutectic can be so obtained in open air only, of course, if the vapor pressure of the system is lower than the atmospheric pressure, as in any salt-water system.

If the salt is added to liquid water, the temperature will fall, but not to the eutectic, for heat must be withdrawn in order to freeze the water. In this case there is no definite temperature reached as a limit, for with three phases (solid salt + liquid + vapor) the system is univariant; even though the atmospheric pressure is constant, the system is not isobaric in respect to the significant partial pressure of water. If, on the other hand, solid CO_2 , with a vapor pressure greater than atmospheric, is added to liquid ether in the open air, a low constant temperature is reached, which is not a eutectic but the boiling point of the saturated solution at atmospheric pressure (schematically, the 3-phase tie-line LVB of Fig. 5-6(e), in which $B = \text{CO}_2$). This temperature is hardly different from the normal sublimation temperature of CO_2 , because the solubility in ether at that temperature is very low; but the "mush" of liquid + solid CO_2 is a more efficient cooling medium for certain purposes than is the solid itself.

E. Critical Phenomenon ($L = V$)

The maximum of the EO_A curve, or the equilibrium ALV, may be so pronounced, in conjunction with a great discrepancy between the triple points of the components and between their critical points, that the solubility curve may intersect the critical curve, $K_A K_B$, of the binary system. This results in two limited ranges of the critical phenomenon on each side of the space model — one near pure A starting from K_A , the other near pure B starting from K_B . Each partial curve is terminated by the intersection with the solubility curve of A, at **critical end-points**, K_1 and K_2 , where the critical phenomenon between L and V involves phases which are at the same time saturated with solid A. Again there are various possibilities depending on the relation between K_A and K_B in respect to both P and T , and on whether the critical curve, assumed uninterrupted, has a maximum or a

minimum in respect to either P or T or both. We shall consider the relations for one example, by means of sections at constant T and at constant P , and the relations for the other possibilities should be apparent through these.

If the solubility of A is always high enough, there may be no interference of its solubility curve with the critical curve even if $K_B < O_A$ in respect to T , as is assumed to be the case in Figs. 5-4, 5-11, 5-13, 5-15. In Fig. 5-16, the solubility curve EO_A is shown intersecting the critical curve; the

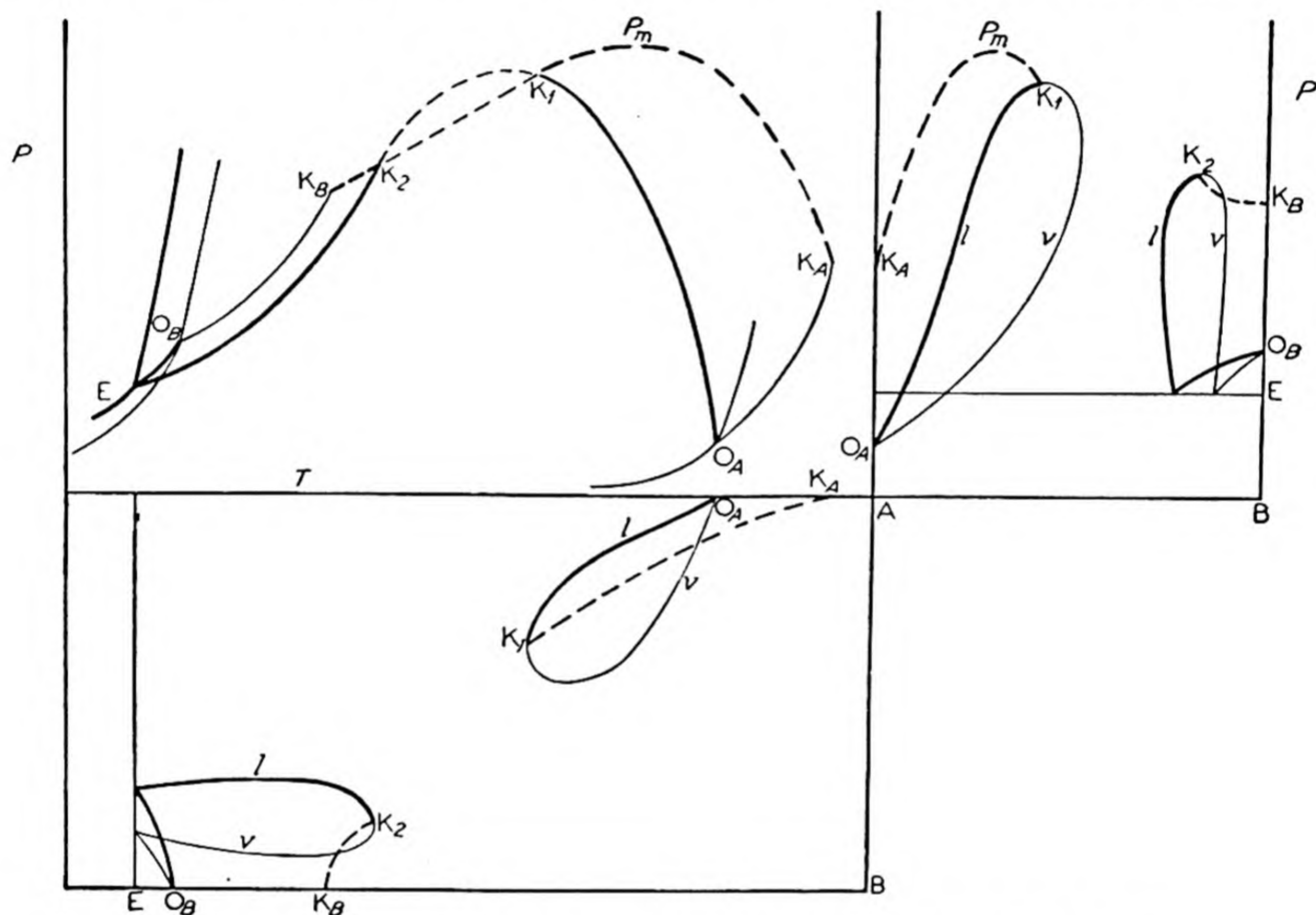


FIG. 5-16. Intersection of solubility curve and critical curve.

system chosen has $K_A > K_B$ in T but $< K_B$ in P , only a pressure maximum in the critical curve, and this maximum, P_m , outside the region of intersection, which lies between points K_1 and K_2 . On the other hand, the pressure maximum of the solubility curve has been assumed to lie within the intersection. The curves (dashed) between K_1 and K_2 , the critical end-points, are, of course, imaginary. Between K_A and K_1 and between K_2 and K_B , the critical phenomenon is the usual one of an unsaturated binary liquid. At the points K_1 and K_2 , the liquid undergoing the critical phenomenon is saturated with solid A, but the two points differ, of course, in respect to P , T , and the composition of the liquid. In each case, as along the curves $K_A K_1$ and $K_2 K_B$, the L and V phases are identical and present in equal amounts. Along the curves, however, the density of the system is a unique function of c (or P or T); but at the points K_1 and K_2 the equilibrium involves a non-critical phase (solid A), the proportion of which may

be varied arbitrarily. These points are singular points, type k . Intersection of solubility curve and critical curve is illustrated by the systems anthraquinone-ether¹⁸ and $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$.¹⁹

Fig. 5-17 shows representative isotherms of Fig. 5-16. The L/V loop becomes detached from the B side at K_B , between 5-17(a) and 5-17(b). In 5-17(b) K marks a point on the critical curve $K_B K_2$, and the L/V loop vanishes at K_2 (Fig. 5-17(c)), at which point the critical phenomenon of the identity of liquid and vapor occurs in presence of solid A. Between K_2 and

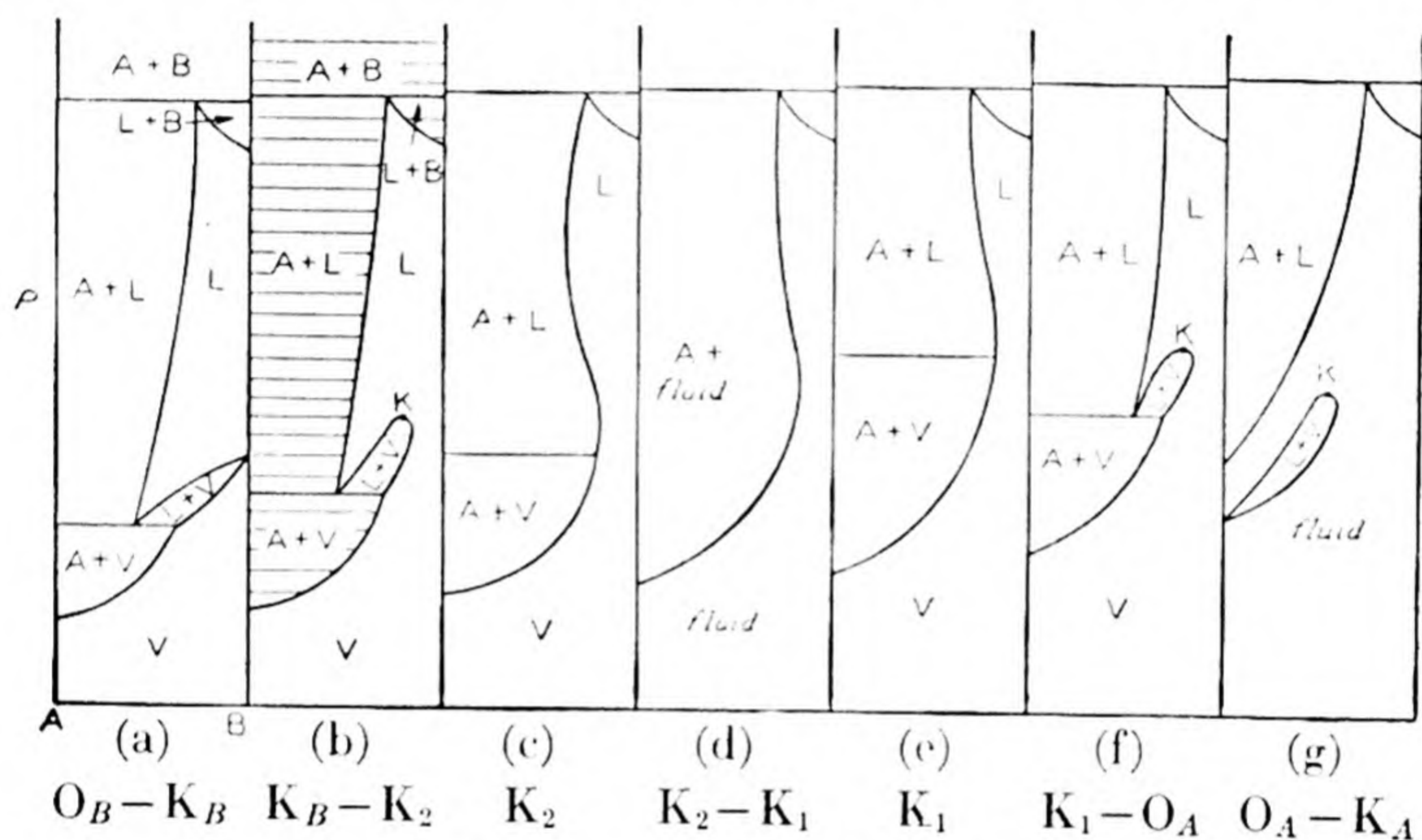


FIG. 5-17. Isotherms of Fig. 5-16.

K_1 (Fig. 5-17(d)) the solubility curve of A is one in which solid A is in equilibrium with a phase which may be called a fluid, since from the lowest P , where it is distinctly a gas, to the highest, where it takes part in the fusion equilibrium ALB, the phase is continuous. This solubility curve is sometimes called the solubility of a solid (A) in a "supercritical gas" (B).²⁰ The L/V loop reappears at K_1 , (Fig. 5-17(e)), where the solid is again in equilibrium with a critical fluid of two identical phases, L and V. The distinctness of the phases increases, with still higher T , the L/V loop reappearing as shown in 5-17(f). In 5-17(g) the triple point of A has been passed, but not its critical point, where the L/V loop will again vanish. If the solubility curve EO_A does not intersect (as in $\text{AgNO}_3\text{-H}_2\text{O}$ or in $\text{NaCl-H}_2\text{O}$ ²¹) the critical curve $K_A K_B$, then all isotherms between K_B and O_A are, schematically, like Fig. 5-17(b).

¹⁸ A. Smits, *Z. phys. Chem.*, **51**, 193 (1905); **52**, 587 (1905).

¹⁹ J. P. Wuite, *ibid.*, **86**, 319 (1914).

²⁰ For some recent examples, see G. A. M. Diepen and F. E. C. Scheffer, *J. Am. Chem. Soc.*, **70**, 4085 (1948).

²¹ M. Étard, *Ann. Chim. Physique*, [7], **2**, 503 (1894).

The isobars are shown in Fig. 5-18. As P rises the L/V loop detaches itself from the A side at K_A , between 5-18(a) and 5-18(b); the same happens at K_B , between 5-18(b) and 5-18(c). As K_2 is approached, the lower loop, that is, that on the B side, diminishes and vanishes at K_2 (Fig. 5-18(d)). At the same time the upper loop has been detaching itself, since it will be left

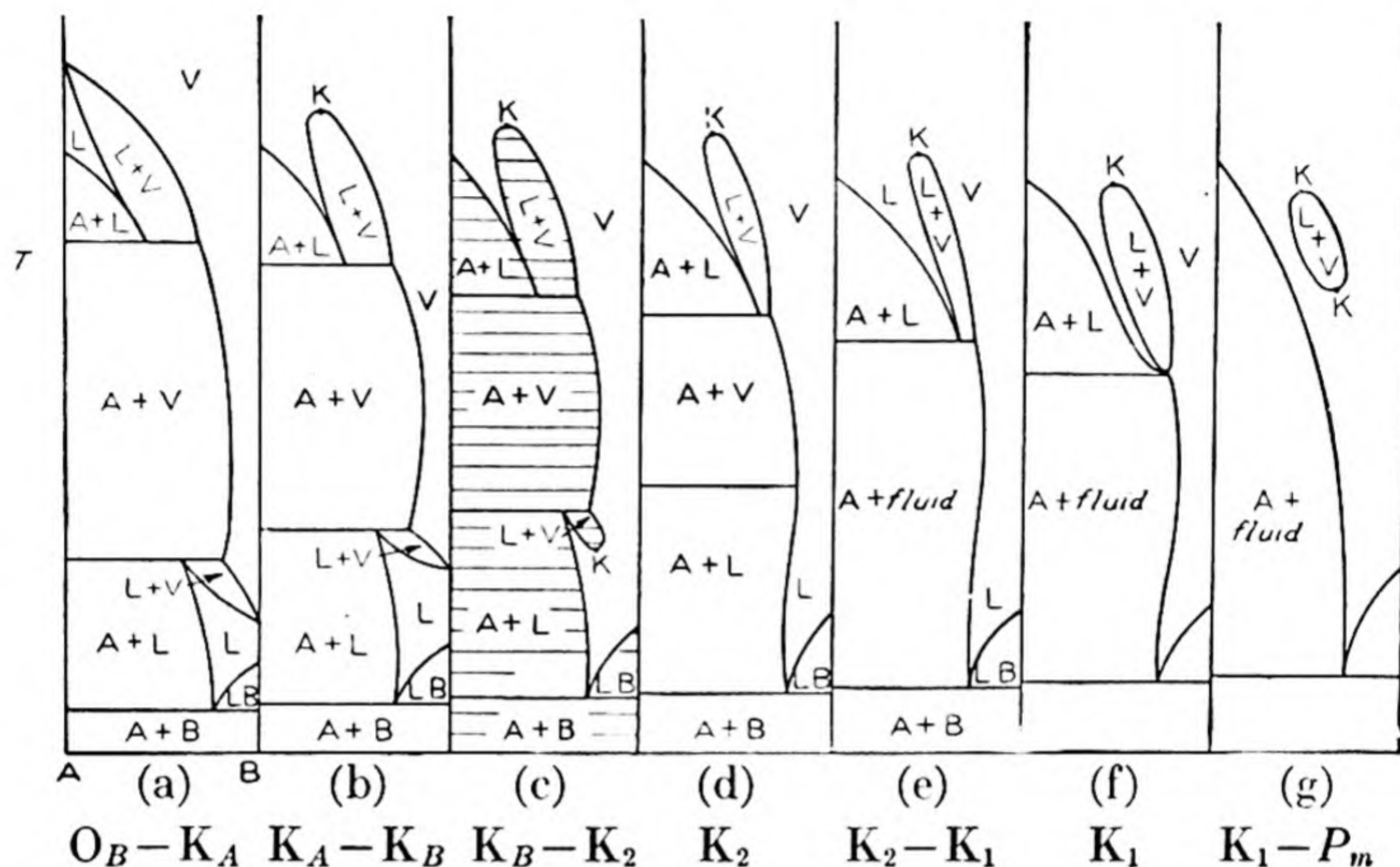


FIG. 5-18. Isobars of Fig. 5-16.

as an “island” in the fluid area, at $P > K_1$ and $< P_m$ (Fig. 5-16). At K_1 it detaches itself from the solubility curve, which thereafter becomes continuous from the fusion temperature of A to the equilibrium ALB. In 5-18(g) we have a closed curve for the equilibrium LV with upper and lower critical points (K, K), finally vanishing at P_m .

F. Aqueous Pressure of Saturated Solutions

1. Deliquescence

If the component B is water, and A a “non-volatile” second component, the vapor pressure curves of Figs. 5-4, 5-11, 5-15 may be taken essentially as the partial pressure curves of water in the atmosphere above the system. If we now take isotherms (a) between E and O_B (0°C) and (b) between O_B (0°C) and O_A , we have Fig. 5-19, in which the composition of the vapor is omitted, since it is assumed to be pure water (B), and in which the pressure is understood to be the partial pressure of water in the atmosphere or in the gas phase (cf. Figs. 5-5(c) and 5-5(e)). If the partial pressure of H_2O in the air, in either case, is P_1 , lower than P_d or that required for the equilibrium ALV, then solid A exposed to air remains dry, the system consisting

simply of $A + V$. But if the aqueous pressure is $P_2 (> P_d)$, the solid **deliquesces**. The only possible system containing the vapor phase, which is required in the open, is now the LV system. Hence the solid, under such an aqueous pressure, takes on water to dissolve in it completely, leaving the unsaturated liquid, or the equilibrium LV, the composition l of the liquid being given by the diagram. The value of P_d is simply the vapor pressure of the EO_A curve of Figs. 5-4, 5-11, 5-15, the solubility curve of A.

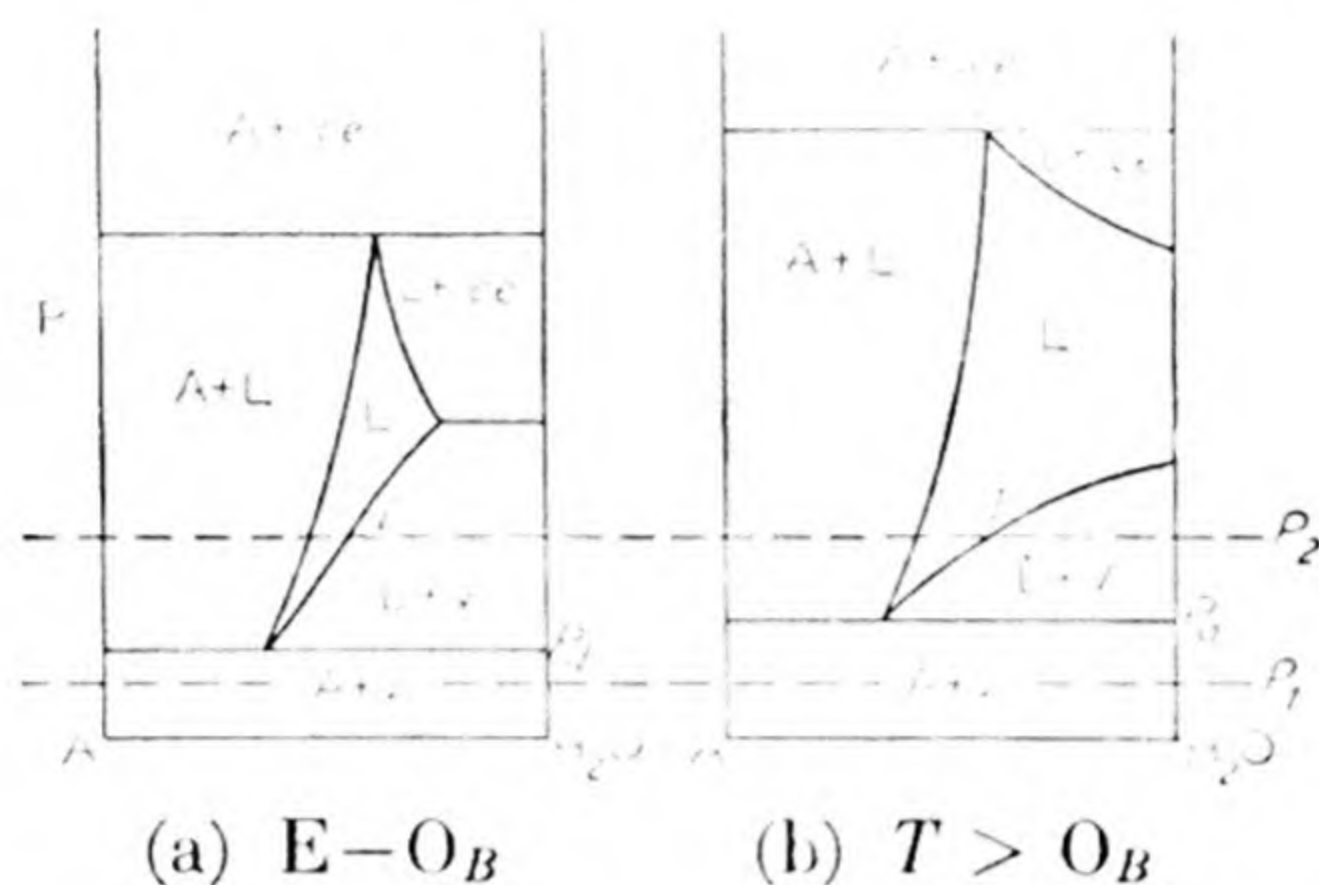


FIG. 5-19. Deliquescence of non-volatile solid A.

In terms of the P/T projection, then, a non-volatile solid does not deliquesce but remains dry if the partial pressure of H_2O in the air is below the curve EO_A at the temperature at which it is exposed, and it otherwise deliquesces (dissolves completely). Since the vapor pressure of the saturated solution EO_A depends primarily on the solubility of the solid A, it is clear that ordinarily (in ordinary air at ordinary T) only very soluble solids will deliquesce. It also follows that the solution of a less soluble solid, having a high aqueous pressure even when saturated, will dry up completely in air, leaving the dry solid, or the equilibrium AV.

2. Desiccants; Hygrostats

From Fig. 5-19 it is seen that an unsaturated aqueous solution l , in equilibrium with the water vapor of the air, has a concentration fixed by its temperature and by the partial pressure of water in the air. A more concentrated solution will take on water, and a more dilute solution will lose water, until this particular concentration is reached. A highly concentrated solution, therefore, with a very low vapor pressure, may be used as a desiccant. Thus considerable amounts of water are taken up by concentrated sulfuric acid, and with hardly any change in its vapor pressure, since the solution may be near the minimum of the $(P/c)_T$ curve of Fig. 3-4(c) (A = sulfuric acid, B = water); in fact there will be a region in which the total vapor pressure, at constant T , falls as water is absorbed.

Since the aqueous pressure of unsaturated solutions at fixed T is a function of the concentration, it is possible, for example, to use sulfuric acid solutions to study the decomposition pressures of hydrates, the vapor pressure being known for the concentration of the acid solution used.²²

A saturated solution on the other hand, or the system $S_A LV$, may be used not only as a desiccant if its vapor pressure is low, but, at constant T , also, in a closed system, as a hygrometer or source of constant aqueous pressure, the pressure depending on the temperature and on the solubility of the solid. As water vapor is absorbed, more liquid of constant composition is formed by dissolving solid, and the vapor pressure is isothermally invariant. Thus if solid A (Fig. 5-19) is enclosed in a space in which the vapor pressure of water is originally greater than the deliquescence pressure P_d (the vapor pressure of the system ALV), the pressure drops to P_d if there is sufficient A to leave excess of solid at equilibrium.

²² H. W. Foote, *J. Am. Chem. Soc.*, **37**, 288 (1915).

Chapter VI Polymorphism of the Components and Pseudobinary Behavior

A. Parallel (or Iso-) Polymorphism, with Complete Miscibility

If the polymorphism of one component, whether enantiotropy or high pressure polymorphism, is paralleled by that of the second component, and if the corresponding forms are completely miscible in each other, no new principle is introduced in the complete phase diagram of the system (Fig. 6-1). If T_A and T_B are enantiotropic transition points of A and B respectively, there will be a binary enantiotropic transition region, shown circling T_A and T_B in the P/T projection of Fig. 6-1, for the 3-phase univariant

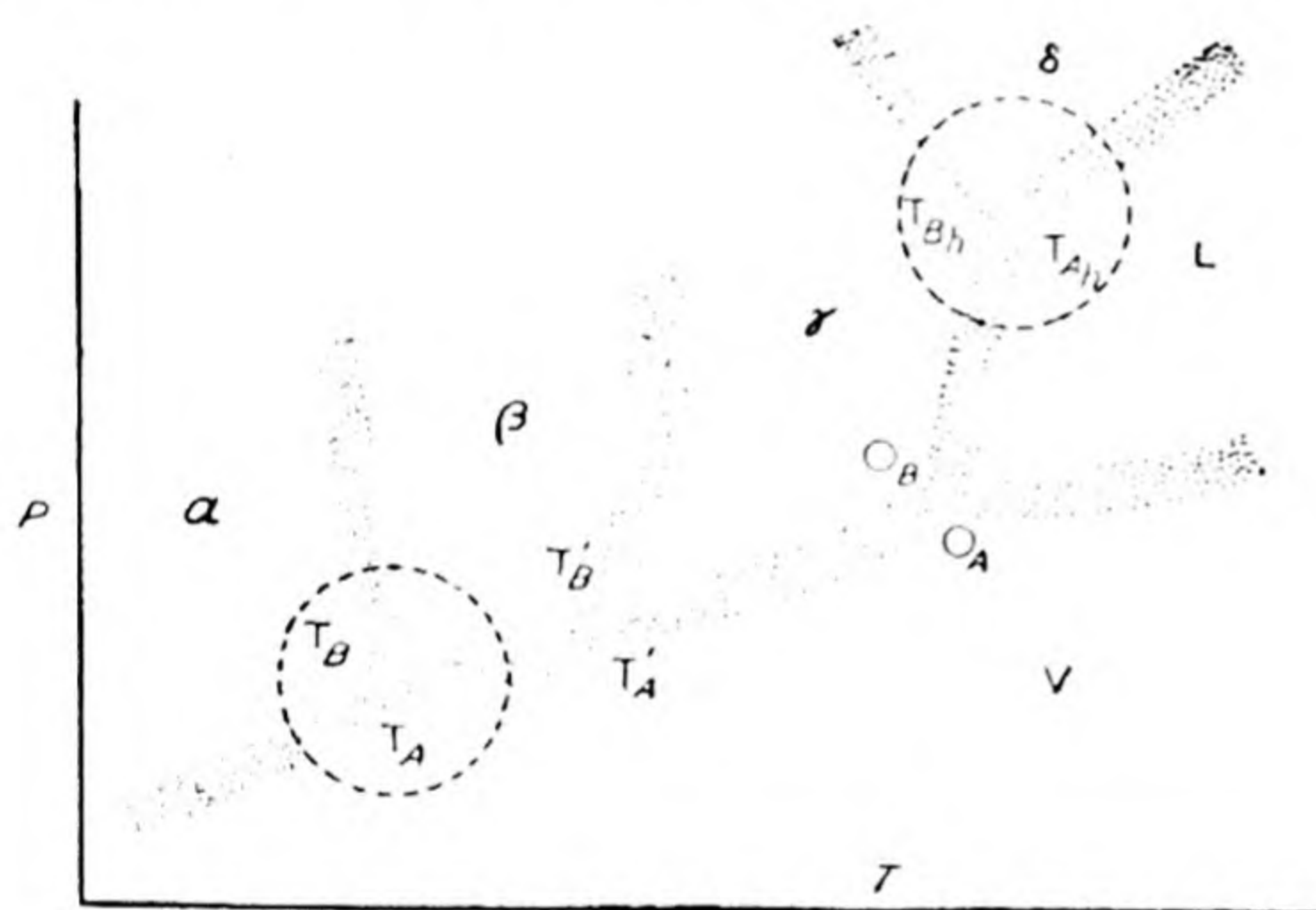


FIG. 6-1. Parallel polymorphism with complete miscibility.

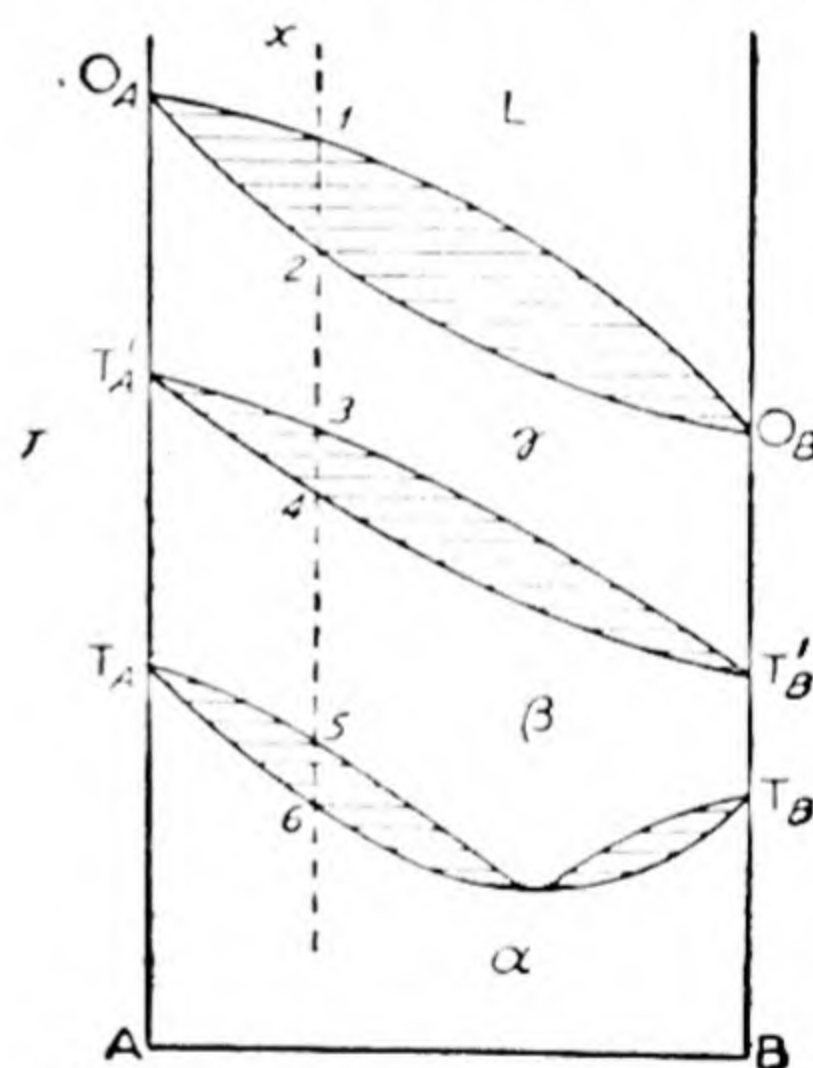


FIG. 6-2. Condensed T/c diagram for Fig. 6-1.

equilibrium involving the phases α , β and V , α being the solid solution of the lower temperature forms, β that of the higher temperature forms. The curves for the three coexisting phases will have the same general relations as the SLV curves of Figs. 3-9 and 3-13 with β in place of L (as observed, for example, for the higher temperature forms in binary systems of some sodium soaps).¹ The same applies to a high pressure transition equilibrium of three condensed phases, such as γ , δ and L , running from T_{Ah} to T_{Bh} , as would be expected in the system H_2O-D_2O .

The "condensed diagram" for a binary system in which the components are completely miscible in every form, with parallel enantiotropy involving

¹ M. J. Vold, M. Macomber and R. D. Vold, *J. Am. Chem. Soc.*, **63**, 168 (1941), for sodium palmitate-sodium stearate.

three forms (which may be true solids or liquid crystals) would be schematically that of Fig. 6-2. The uppermost loop is the melting point equilibrium, between solid solution γ and liquid, running between the melting points O_A and O_B . The next are transition loops, representing the transition between solid solutions. The relations between γ and L on the first loop are analogous to the relations between β and γ on the second. The system is homogeneous (single condensed phase) between these loops, and heterogeneous, represented by horizontal tie-lines, inside them. As the liquid x is cooled, it freezes over a melting range (T_1 - T_2) while it passes through the first loop, as explained in connection with Fig. 3-3(b). The solid solution γ (composition x) then undergoes transition to solid solution β over the transition range T_3 - T_4 ; and finally between T_5 and T_6 there is a further transition to solid solution α , the lowest temperature form. These transition loops may involve minima or maxima, with relations like those explained under Fig. 3-4.

B. Non-Parallel Enantiotropy, with Complete Miscibility

If the enantiotropy is not parallel, a 4-phase quadruple point, involving either three solids and vapor or two solids, liquid, and vapor, may appear even without a miscibility gap in any form. The condensed diagrams of Fig. 6-3 show some of the possibilities. In Fig. 6-3(a) (example, HgI_2 - HgBr_2 ²) either the $\alpha\beta$ transition point for component B does not exist or it occurs at too low a temperature for detection. Although the solid miscibility then is presumably unlimited, the enantiotropy is in the practical sense non-parallel. Fig. 6-3(b) is similarly non-parallel, with three forms for A and only one for B. In this diagram both transition temperatures of A, T_A and T_A' , are lowered by the component B. In 6-3(c) it is assumed that T_A is raised while T_A' is lowered, with the result that the field of the solid form β is confined to a closed bulge or loop between T_A and T_A' . This can happen only when the two forms α and α' of component A are structurally the same phase, as is the case for iron (Fig. 2-11), the phases alpha-ferrite, gamma-ferrite, delta-ferrite corresponding to the schematic forms α , β , α' of Fig. 6-3(c). If the upper transition temperature T_A' is raised, the $\beta\gamma$ transition equilibrium comes to intersect the γL melting equilibrium at a quadruple point Q (Fig. 6-3(d)), involving the phases $\gamma\beta LV$. This is a peritectic type of invariant, very similar to that of Fig. 4-12(a). But whereas the S_1 and S_2 fields of 4-12(a) represent the same

² W. Reinders, *Z. phys. Chem.*, **32**, 494 (1900). With T_A at 127° , the lower part of the diagram was established through ternary solubility studies by means of acetone or 95% alcohol as solvent.

phase, split by a miscibility gap, we are here dealing with a transition between two structures, β and γ . Nevertheless, if the transition temperature T_A' of the present diagram should be too low for detection, the two cases could be distinguished only through structural analysis, not on the basis of the phase diagram alone.

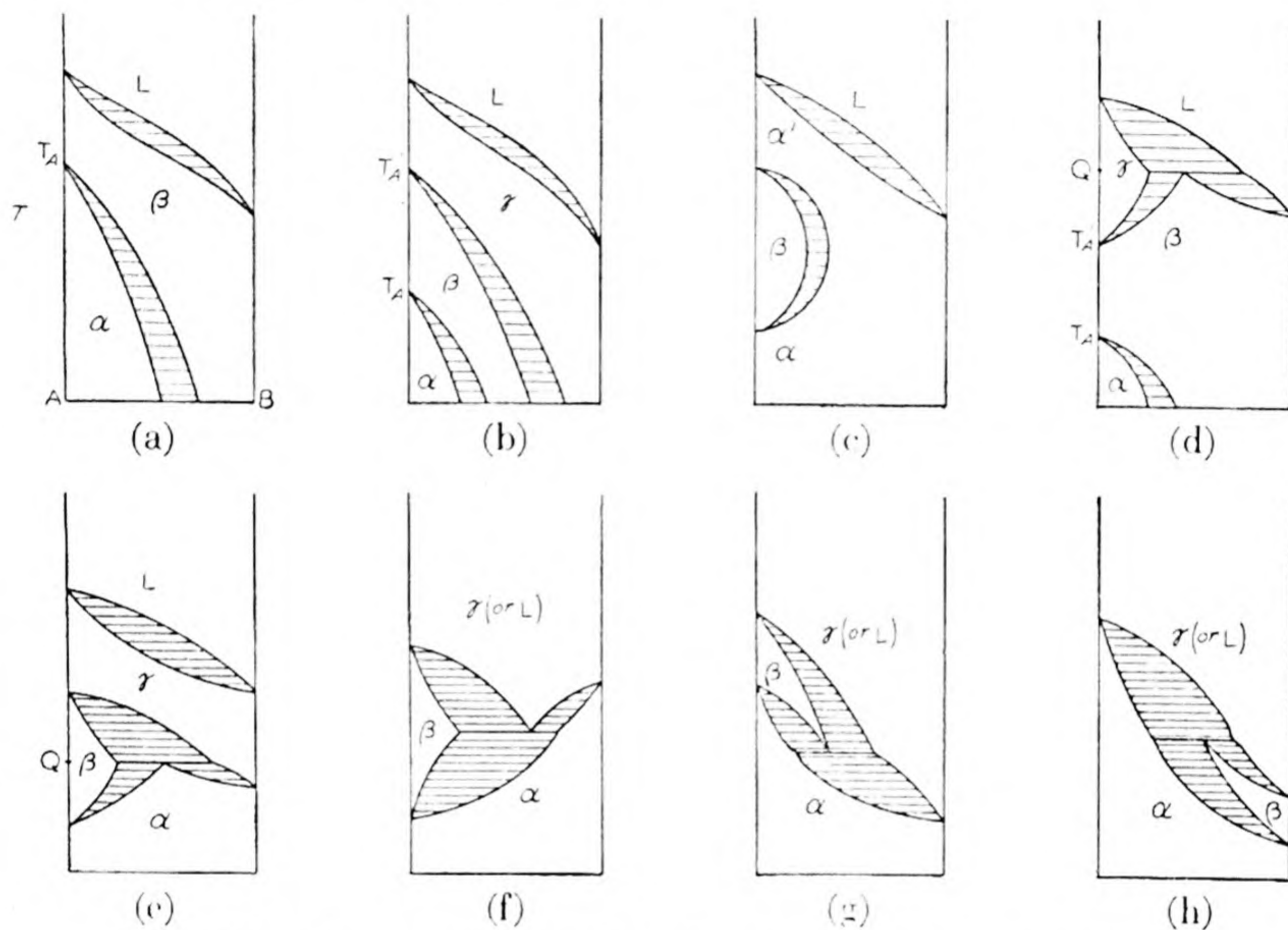


FIG. 6-3. Non-parallel enantiotropy with complete miscibility.

In Fig. 6-3(e) the point Q is a similar invariant equilibrium involving the phases $\beta\alpha\gamma V$, so that it differs from that of Fig. 6-3(d) only in having the solid γ in place of the liquid. Hence the remaining cases, Figs. 6-3(f, g, h), are labeled as applying to either γ or L as the uppermost condensed phase.

C. Miscibility Gap in One or More Forms

If the components are completely miscible in the higher temperature form β , with a *MG* in the lower form α , the fundamental relations are shown in the condensed diagrams of Fig. 6-4. In Fig. 6-4(b), both transition temperatures, T_A and T_B , are lowered, and in Fig. 6-4(a), that of A is lowered while that of B is raised. The transition diagrams are seen to be entirely similar to melting point diagrams for complete miscibility in the liquid state (β in place of L) and incomplete miscibility in the solid state, the two solid solutions here being α_1 and α_2 of the lower forms (A_α and B_α)

of the components. The solid solution e , form β , of Fig. 6-4(b) is in equilibrium with the solid solutions a and b of form α . With the vapor, this constitutes an invariant quadruple point known as a **eutectoid**. At a (binary)

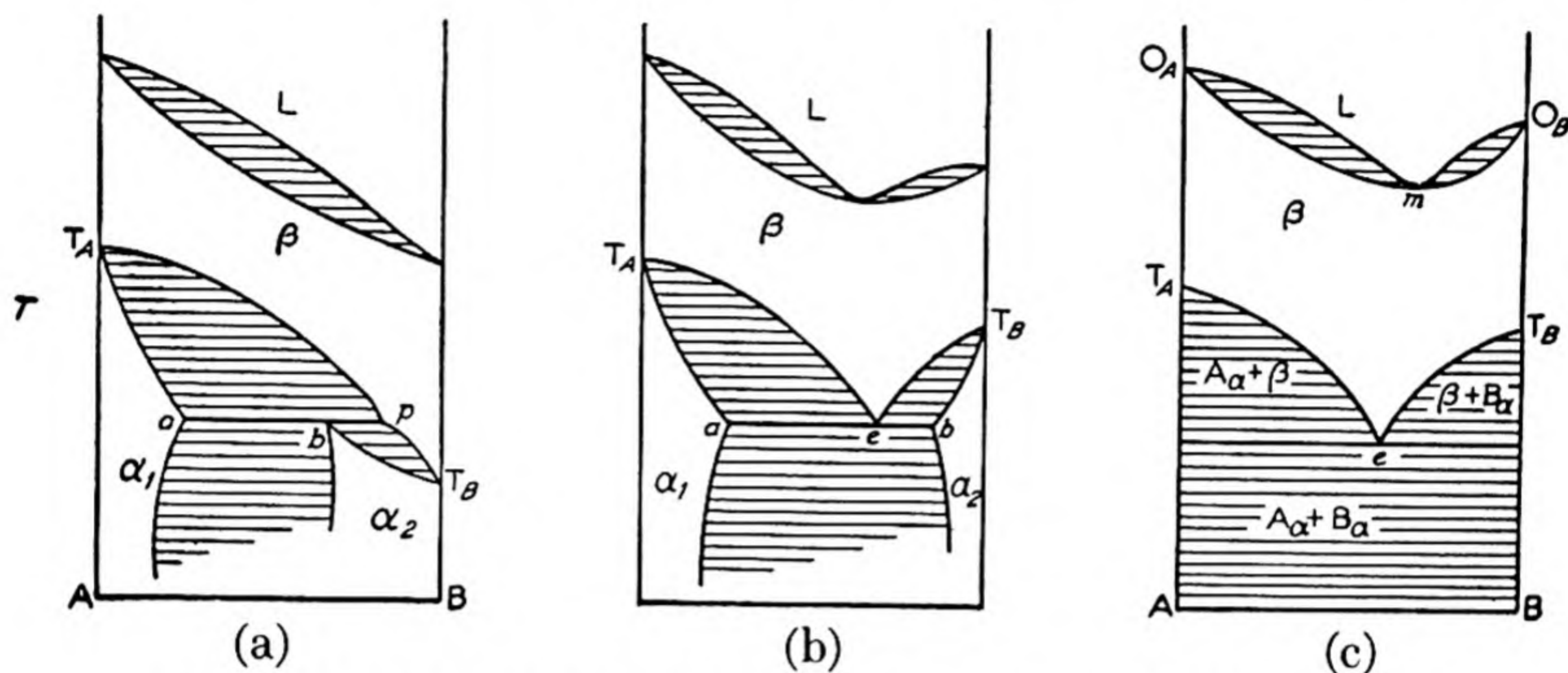


FIG. 6-4. Peritectoid and eutectoid, condensed diagrams.

eutectic a liquid freezes invariantly to a mixture of two solids; at a (binary) eutectoid a solid solution (e) is said to be “resolved” into two other solids, here a and b . Fig. 6-4(a), on the other hand, is a **peritectoid** system. If a solid solution of the upper form β , with composition between a and p , is cooled below the transition curve T_{Ap} , it becomes heterogeneous, giving two solid solutions defined by the curves T_Aa for α_1 (lower form) and

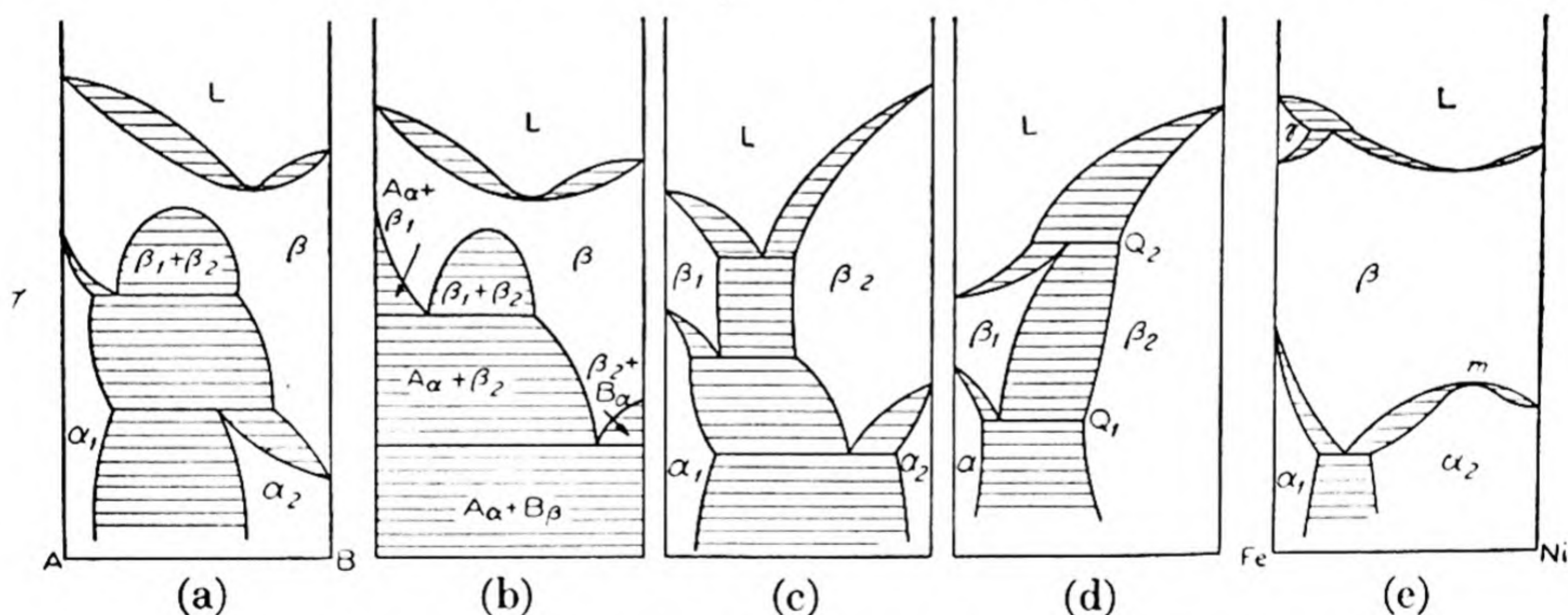


FIG. 6-5. Transitions and miscibility gaps in solid state.

T_{Ap} for β (upper form). At the peritectoid temperature, that of the quadruple equilibrium of three solid solutions, a , b , p , and vapor, the system is invariant while the third solid solution b (of the lower form α_2) appears. If the total composition falls between a and b , the original solid solution now disappears completely, with the composition p , leaving, as conjugate solid solutions, a and b , both of the lower form of the system, α_1 and α_2 .

If the lower forms A_α and B_α are immiscible, then the system is always eutectoid in type. Fig. 6-4(c) represents schematically the system *p*-methoxycinnamic acid (A) and *p*-azoxyanisole (B), the continuous β phase being liquid crystalline; the temperatures involved are $O_A:186$, $m:132$, $O_B:135$, $T_A:171$, $e:108$, $T_B:114^\circ$.³

Some other possibilities are illustrated in the schematic diagrams of Fig. 6-5, which should be self-explanatory. The diagram of Fig. 6-5(c) represents the system $\text{TiNO}_3(\text{A})\text{-KNO}_3(\text{B})$ ⁴; Fig. 6-5(d), the system $\text{NaNO}_3(\text{A})\text{-AgNO}_3(\text{B})$ ⁵; and Fig. 6-5(e), the system Fe-Ni .⁶

D. The Binary Transition Point; Quadruple Point $\alpha\beta$ LV

We shall now consider the quadruple point of Fig. 6-3(d) for the case in which the solid miscibility in the lower form β is limited or entirely absent. We shall assume, in fact, in Fig. 6-6, that the component A alone is enan-

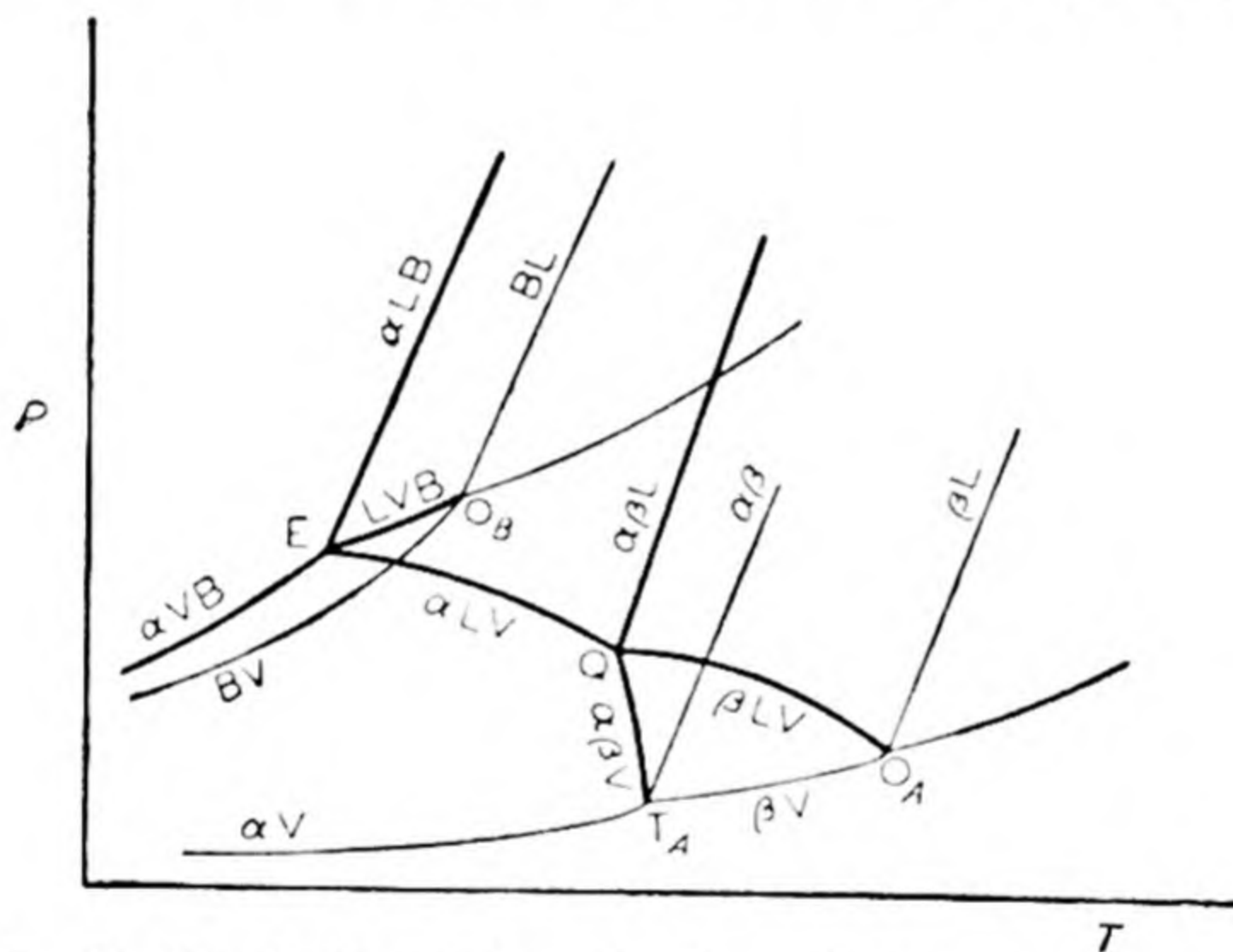


FIG. 6-6. P/T relations for the invariant point Q, or $\alpha\beta$ LV.

tiotropic, with forms α and β , and with the transition point T_A high enough in temperature to affect the liquid solubility curve of the component. This means that there will be a quadruple point, Q, involving L, V, and the two forms of A, above the eutectic or peritectic point of the binary system. The 3-phase, binary transition curve $\alpha\beta V$, originating at T_A , cuts the solubility curve of β , βLV , before it reaches the peritectic or the eutectic with B. The P/T projection of Fig. 6-6 shows the eutectic case, but the

³ A. C. de Kock, *Z. phys. Chem.*, **48**, 129 (1901); for further cases, see A. Prins, *ibid.*, **67**, 688 (1909).

⁴ C. Van Eyk, *Z. phys. Chem.*, **30**, 430 (1899).

⁶ D. J. Hissink, *ibid.*, **32**, 537 (1900). The temperatures of Q_1 and Q_2 are 138 and 217.5°, respectively. The relations below Q_1 were established through the study of the solubilities in a ternary system consisting of NaNO_3 - AgNO_3 and aqueous alcohol of such strength as to give solubilities suitable for accurate analysis.

⁶ Hansen, *loc. cit.*, p. 696.

relations at Q are essentially the same in the peritectic case. Fig. 6-7 shows the T/c projections of such a system; in 6-7(a), the transition temperature T_A is assumed to be lowered, in 6-7(b) raised, by B ; but in both cases, solid A_α and solid A_β are assumed to dissolve B to some extent. In 6-7(c) on the other hand, all the solids are assumed pure.

The point Q , which appears as a break in the solubility curve, where the solid phase changes from α to β , is the intersection not only of the three vapor systems ($\alpha\beta V$ from T_A to Q , βLV from O_A to Q , αLV from E to Q) shown in T/c projection in Figs. 6-7(a) and (b), but also of the system $\alpha\beta L$, not shown in Fig. 6-7, rising to high P from Q itself.

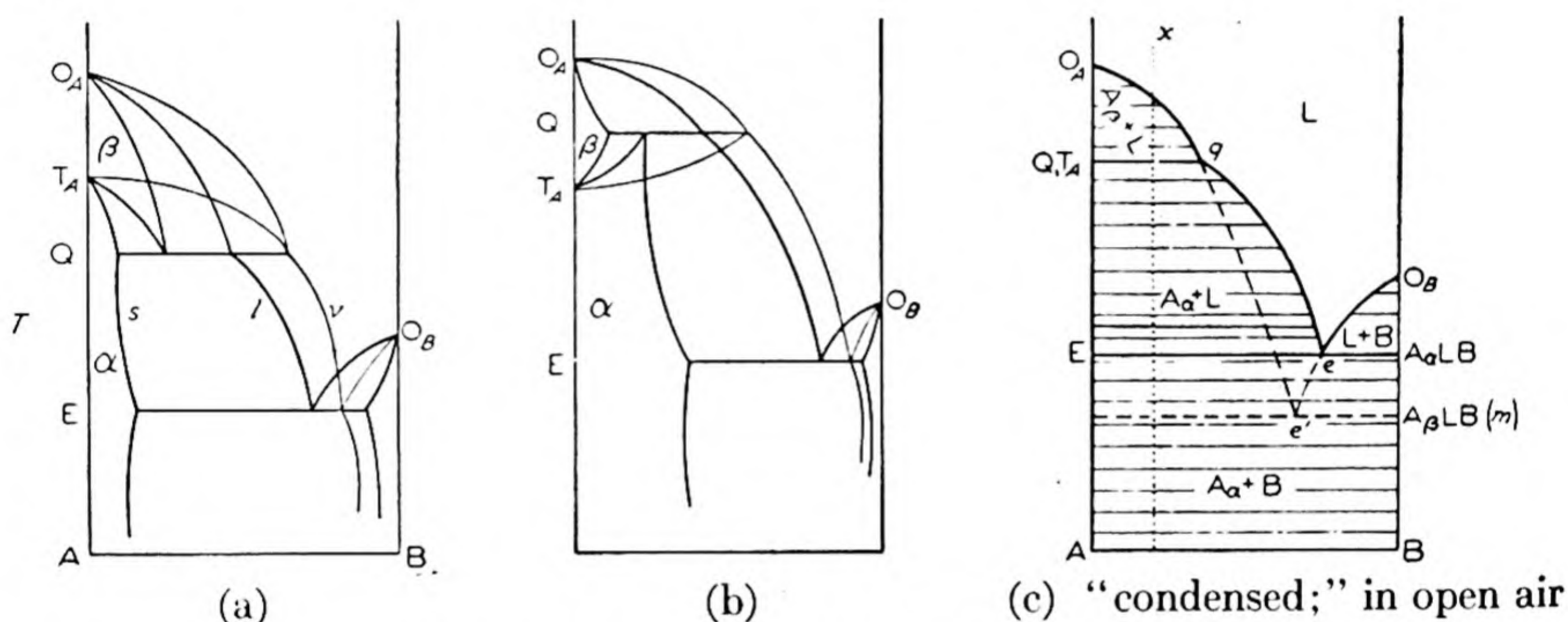


FIG. 6-7. T/c projections for Fig. 6-6.

If the solids are not pure, the point Q may be higher or lower than T_A in respect to P or T or both, regardless of the slope of the unary transition curve $A_\alpha A_\beta$ originating at T_A and rising to high P . If the solids (A_α and A_β) are pure, however, the pressure of Q must be higher than that at T_A because the curves $\alpha\beta V$ (from T_A to Q) and $\alpha\beta L$ (originating from Q to high P) must be coincident, in the P/T projection, with the transition curve $A_\alpha A_\beta$ of the pure component. Then the temperature of Q will be higher or lower than that of T_A depending on the slope of this unary transition curve. In this case, then, the "normal" transition temperature T_A for the unary system determined in open air will be identical with the temperature of Q in the condensed binary system similarly determined in the open air, even if air dissolves in the liquid phase, as explained in Chapter I, Section H-3. If the solids are pure, therefore, the point Q of the open-air binary system gives the normal transition temperature T_A of the component A .

If the binary solution x (Fig. 6-7(c)) is cooled, it precipitates A_β on reaching the liquidus (freezing point or solubility curve) $O_A q$. At the temperature Q the system is invariant with vapor present (or isobarically

invariant), and the temperature and the concentration of the solution (and vapor) remain constant while A_β is transformed to A_α . The solution, however, is not only invariant in composition during the phase reaction, but also constant in actual amount, since the component B, not involved in the solid phase changes, is entirely contained in the invariant liquid. The system in the present case is formally binary, but the phase reaction at Q, for the case of pure solids, is unary. As pointed out in section H-3 of Chapter I, some phase is always constant in quantity during a phase reaction of *lower order*.

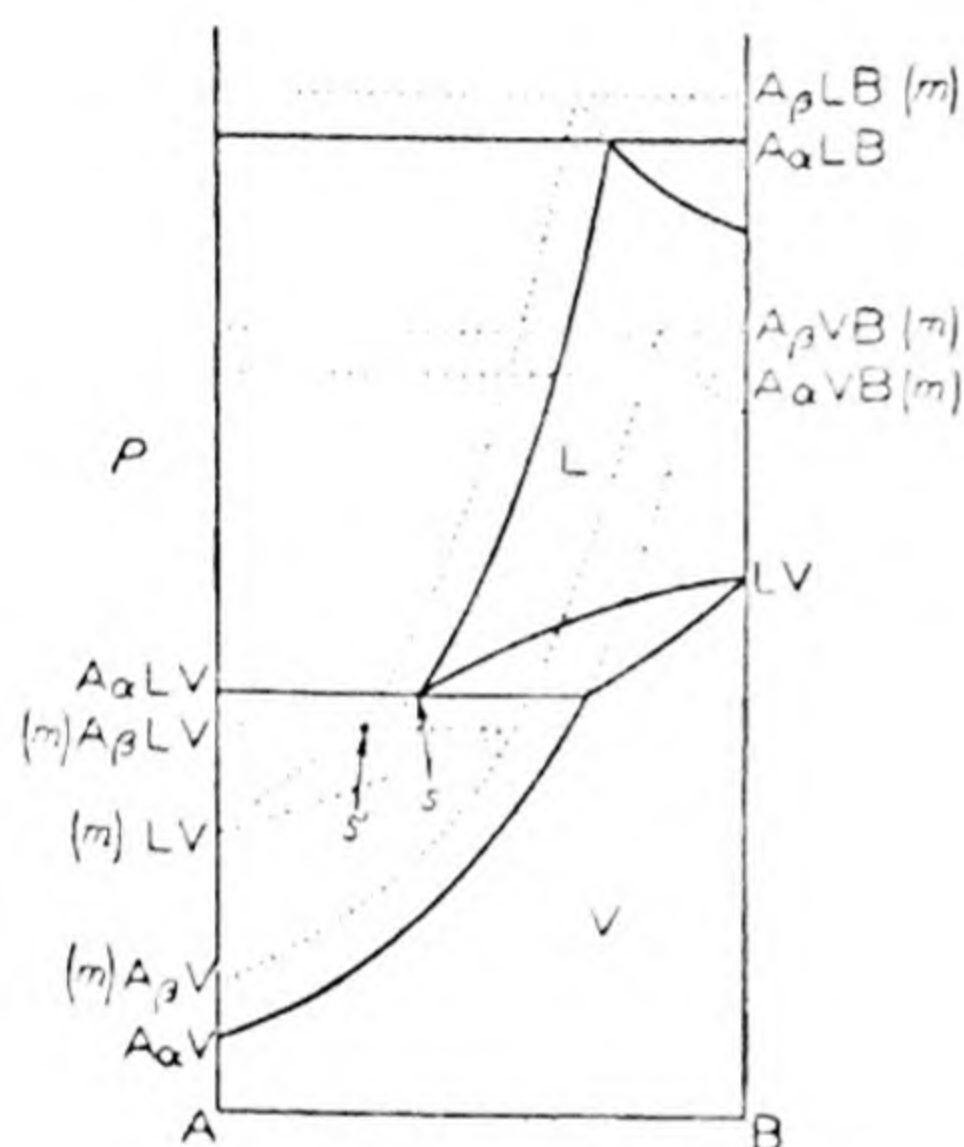


FIG. 6-8. Isotherm of Fig. 6-6, $O_B - T_A$, for pure solids.

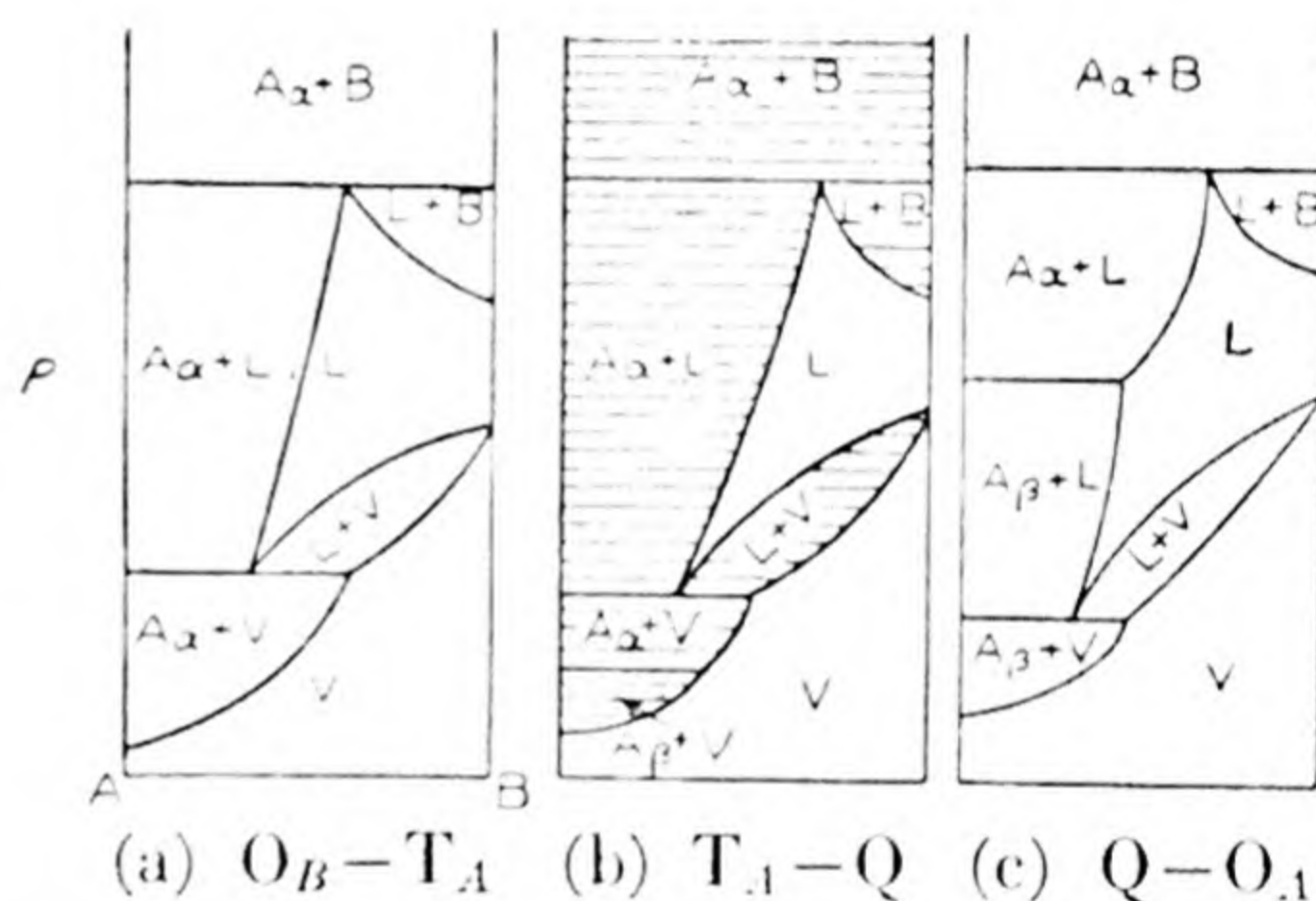


FIG. 6-9. Isotherms of Fig. 6-6, for pure solids.

When the transition is complete the system consisting of $A_\alpha + L(+V)$ proceeds to the eutectic in the usual way. If the transition point Q is passed and the A_β form continues metastably below it, its own solubility curve would be followed, as a metastable equilibrium curve, until it intersects the freezing point curve of B at a metastable eutectic (e'). Since the solubility of the metastable form is greater than that of the stable form at the same T , the metastable eutectic temperature is lower than the stable one, and the composition e' is normally to the left of e .

The solubilities of the two forms, at a specified value of T , are related to their vapor pressures. Fig. 6-8 is an isothermal section of Fig. 6-6 between O_B and T_A , for pure solids and for positive P/T slope of the transition curve $A_\alpha A_\beta$. Below T_A the vapor pressure of solid A_β (metastable) is higher than that of A_α (stable). The solubility of a form at specified T is the concentration (s for A_α) of the liquidus of the L-V loop at the pressure where the vaporus of the S-V loop crosses the vaporus of the L-V. It is seen, consequently, that the form A_β with the higher vapor pressure at the

specified T crosses the L/V vaporus at a lower P , and hence at a higher concentration of A in the liquid (s'). At this temperature, therefore, the vapor pressure of solid A_β exceeds that of solid A_α , but the vapor pressure of the saturated solution of A_β , because of its higher solubility, is lower than that of the saturated solution of A_α . Fig. 6-8 shows two sets of equilibrium curves for each of the equilibria solid-liquid and solid-vapor, one for each solid form of A, but only one LV curve since the polymorphism is limited to the solid state.

For pure solids, in which the curves $\alpha\beta V$ and $\alpha\beta L$ of Fig. 6-6 are coincident, in P/T , with the curve $A_\alpha A_\beta$ of pure A, Fig. 6-9 shows isotherms at (a) between O_B and T_A , (b) between T_A and Q , and (c) between Q and O_A ; the P/T slope of $A_\alpha A_\beta$ is assumed positive again. Fig. 6-10 shows isobars, (a) between O_A and Q , and (b) between Q and E .

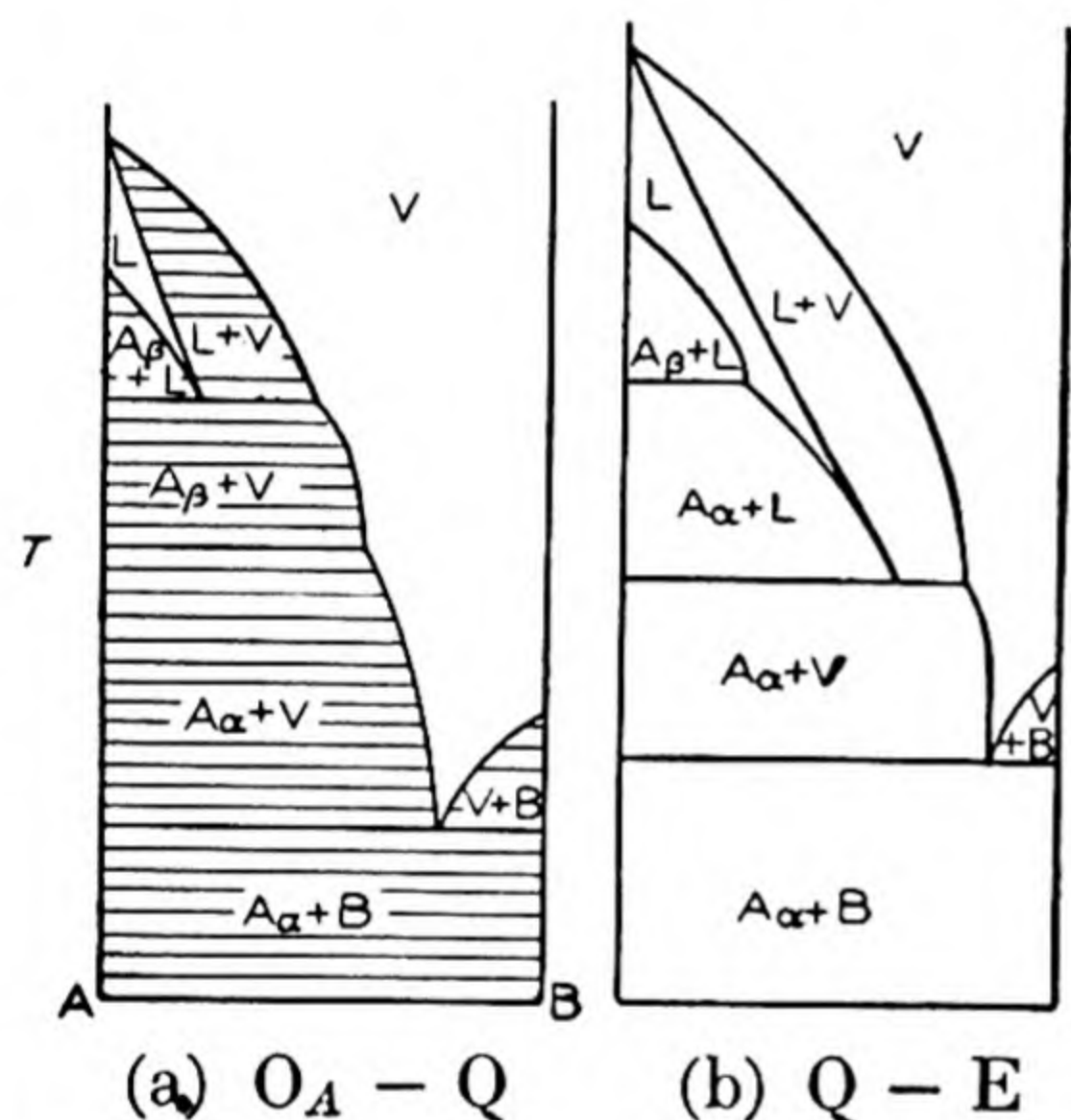


FIG. 6-10. Isobars of Fig. 6-6, for pure solids.

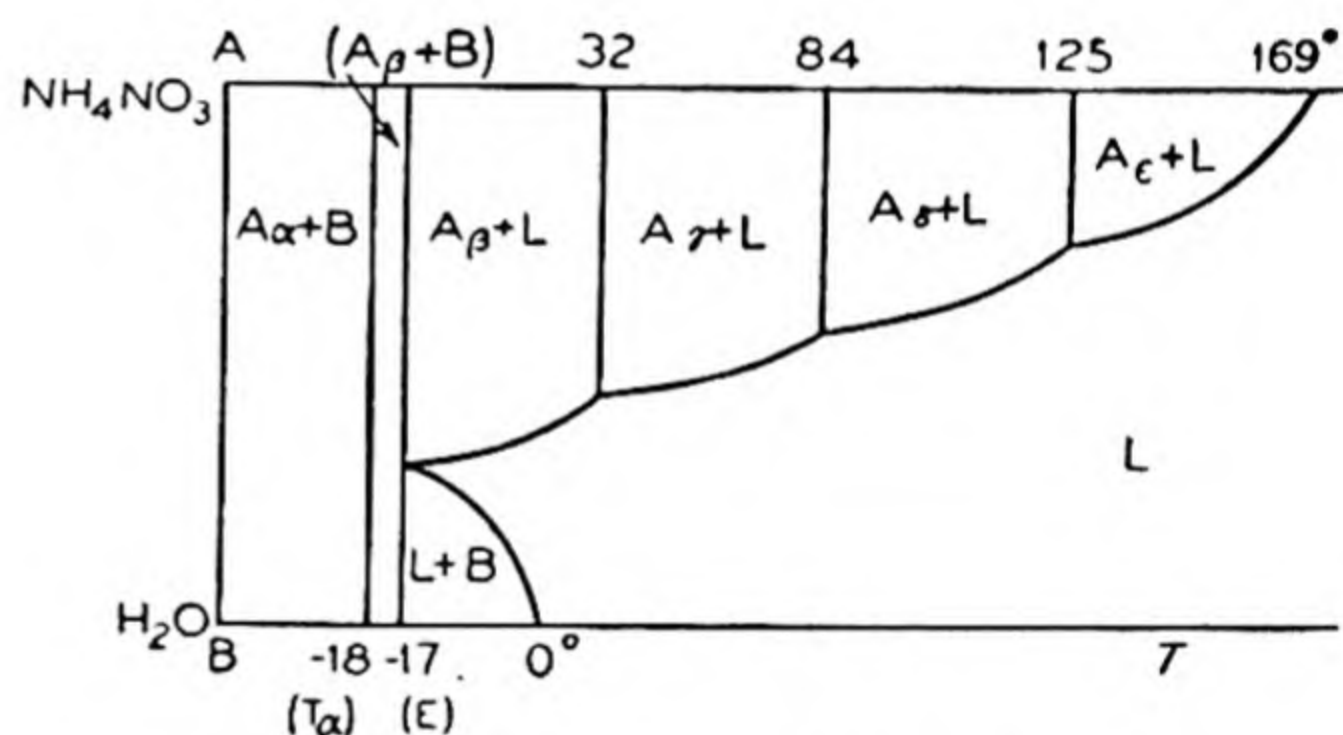


FIG. 6-11. System $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$ (condensed, schematic).

If there is a series of enantiotropic transitions for A, there will be a series of quadruple points, appearing on the condensed diagram as in Fig. 6-11 for the system $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$ (schematic). Any further enantiotropic transitions of A below the eutectic would appear as straight lines across the diagram, as at T_α , for a transition between the two lowest forms, A_α and A_β , of NH_4NO_3 (the eutectic is reported at -16.8° ; the lowest polymorphic transition at -18.0°).⁷

As in the case of Figs. 5-11 and 5-15, each of the vapor pressure curves for solutions saturated with the various enantiotropic forms of the component A, such as curves EQ and QO_A of Fig. 6-6, may pass through a maximum in pressure. In the case of the system $\text{AgNO}_3\text{-H}_2\text{O}$ only the

⁷ I. C. T., IV-217.

solution saturated with respect to the higher temperature modification, or $\beta\text{-AgNO}_3$, passes through such a maximum.⁸ In the system $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$ there are vapor pressure maxima both for the solution saturated with $\delta\text{-NH}_4\text{NO}_3$ and for that saturated with $\epsilon\text{-NH}_4\text{NO}_3$.⁹

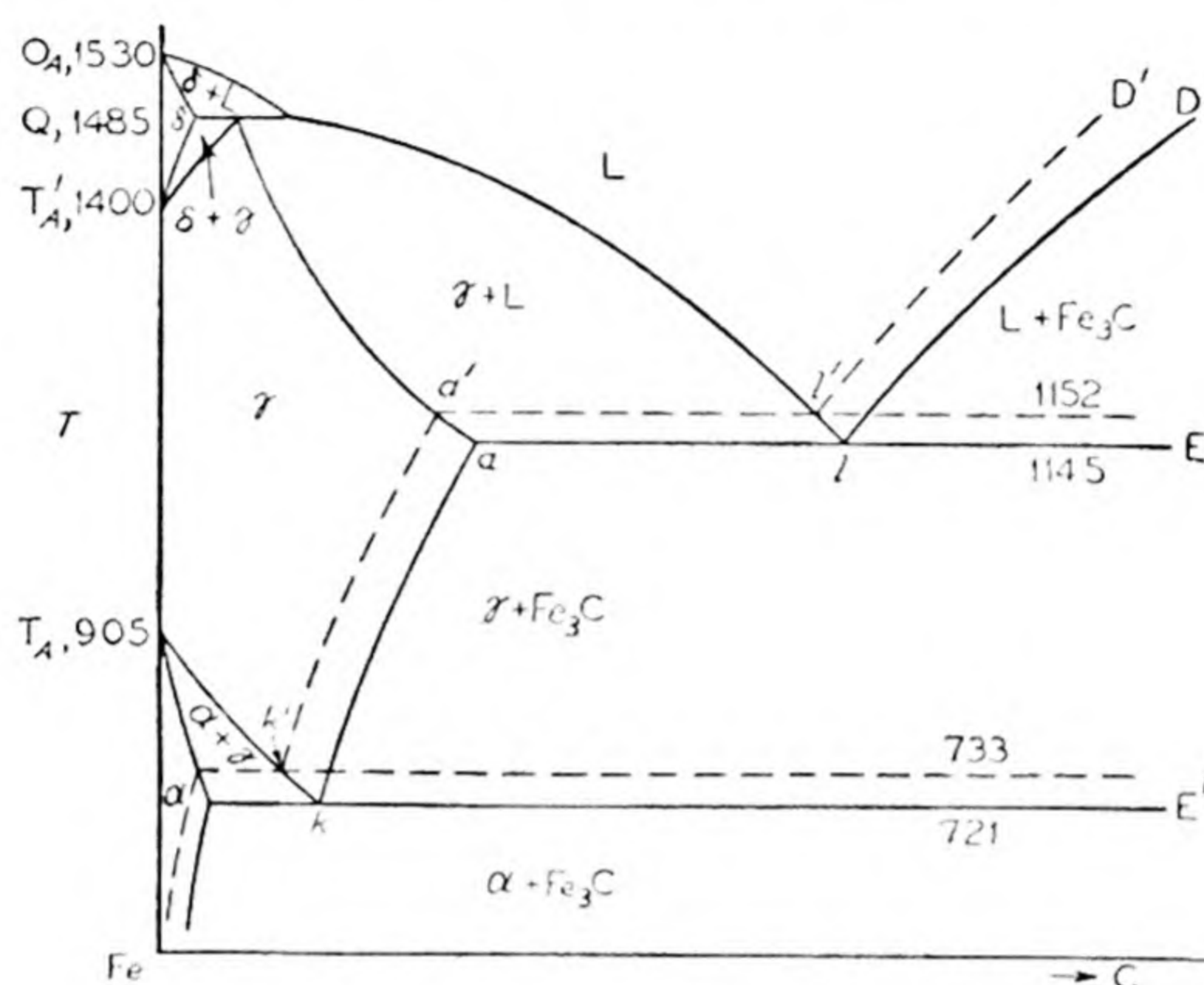


FIG. 6-12. System iron-carbon (schematic).

Figs. 6-9 to 6-11 involve no solid solution. The system Fe-C (Fig. 6-12 (schematic)), is an important example of non-parallel enantiotropy with solid solution. O_A is the melting point of iron (δ form), and T_A' and T_A are the upper and lower transition temperatures of γ -iron, separating the two parts of the other form of iron (α and δ), as discussed in Chapter II. Each solid phase, here labeled simply δ , γ , α , is a solid solution of carbon in iron, although the carbon content of the α phase is extremely low. Since α and δ are of the same form, and hence, in a sense, parts of the same phase, the effect of a second component, "B", upon the diagram Fe-"B" will depend on the relative solubility of "B" in the two phases γ and α - δ .¹⁰ If the solid-solubility of "B" in the $\alpha\delta$ phase is small, but large in γ , the "B" component will tend to expand the field of existence of the latter at the expense of the former. Thus carbon raises the $\delta\gamma$ transition temperature and lowers the $\gamma\alpha$ transition temperature, with the effect seen in Fig. 6-12. Point Q is a quadruple point (the vapor is not shown in the diagram) of the type of that of Fig. 6-7(b); and point E' is a eutectoid, as in Fig. 6-4(b) or (c). Point E is a eutectic, the liquid l of minimum freezing point being

⁸ P. Dingemans and K. van den Berg, *Rec. trav. chim. Pays-Bas*, **61**, 605 (1942).

⁹ P. Dingemans, *ibid.*, **60**, 317 (1941).

¹⁰ The relation may also be expressed in terms of the free energy change in the process of solution; see C. Zener, *Am. Inst. Mining Met. Engrs., Metals Technol.*, **13**, no. 1, Tech. Pub. No. 1856 (1946).

in equilibrium with a γ solid solution of maximum carbon content, a , and a second solid phase, iron carbide or cementite, Fe_3C . The term "austenite" is frequently applied to γ solid solutions, produced at equilibrium in the γ field of Fig. 6-12. All the relations shown in this figure refer, of course, to equilibrium conditions, and the actual product on cooling complexes of various compositions from various temperatures depends on operational variables, as in any system: degree of attainment of equilibrium at the original high T , the direction of approach to equilibrium, in respect to T and c , and the rate of cooling. Moreover, the relations represented by the curves $Dlak$ of this figure are metastable with respect to the set of curves labeled $D'l'a'k'$, which involve saturation with the stable phase graphite.

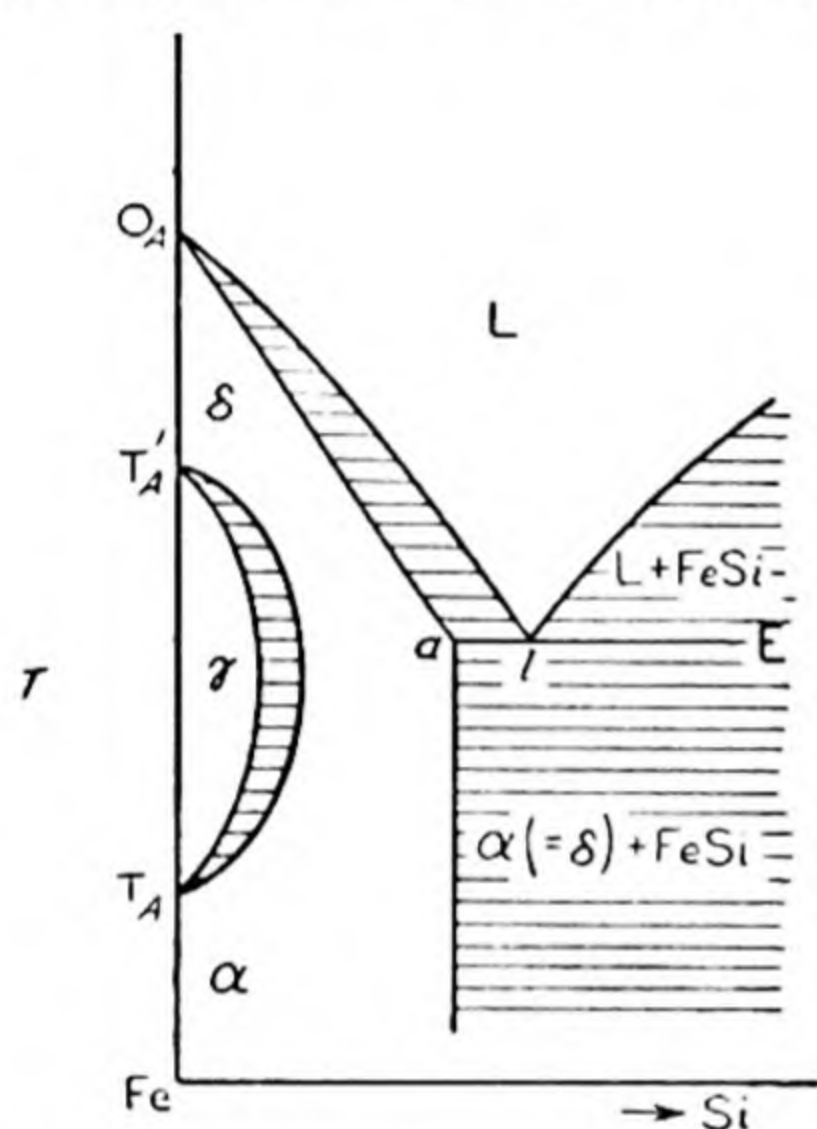


FIG. 6-13. Portion of iron-silicon diagram (schematic).

The latter equilibrium, however, is less readily attainable than that with cementite, which is therefore to be considered the diagram of greater practical importance.^{10a}

If the solid-solubility of the second component in the $\alpha\delta$ phase is high, and low in γ , T_A is raised and T_A' is lowered, so that the γ field shrinks. Now it is possible for the α and δ regions to become so enlarged as to coalesce, thereby isolating the γ field, as already mentioned under Fig. 6-3(c). This occurs in the "loop systems" or "bulge systems" Fe-Si, Fe-Sn, Fe-Cr, so-called from the shape of the γ field. Schematically, Fig. 6-13 shows the Fe side of the system Fe-Si. Here the eutectic involves an (α, δ) solid solution, a , instead

of the γ phase. Boron similarly contracts the γ field, but without causing the α and δ fields to merge. Nickel and copper, like carbon, expand the γ field. Zirconium has the unusual effect of lowering both transition points, T_A and T_A' .^{10b}

E. High Pressure Quadruple Points Involving Liquid

Three examples of binary transition points (quadruple) involving two forms of a component, a liquid, and a second component will be discussed. For simplicity we shall assume all the solids to be pure and the systems therefore of the eutectic type.

^{10a} Cf. Tammann (Ref. P-1), pp. 234-253. For the temperatures and concentrations, see S. Epstein, *The Alloys of Iron and Carbon*, McGraw-Hill, N. Y., 1936, p. 157; and Hansen, *loc. cit.*, p. 361. According to C. Wells, *Amer. Soc. Metals*, **26**, 289 (1938), however, cementite does become the stable solid phase in equilibrium with liquid at some temperature slightly above the eutectic.

^{10b} For these binary diagrams involving iron, see Hansen's book, *loc. cit.*

1. If the component A has an enantiotropic transition point above the eutectic of the system (Fig. 6-6), the equilibrium $A_\alpha A_\beta L$ originating at Q is, as already pointed out, coincident with the unary transition curve $A_\alpha A_\beta$. If, then, the slope of this transition curve is sufficiently positive (as in the case of sulfur, Fig. 2-8), we may have the relations shown in Fig. 6-14, in which the equilibrium $A_\alpha A_\beta L$ is terminated at the unary triple point invari-

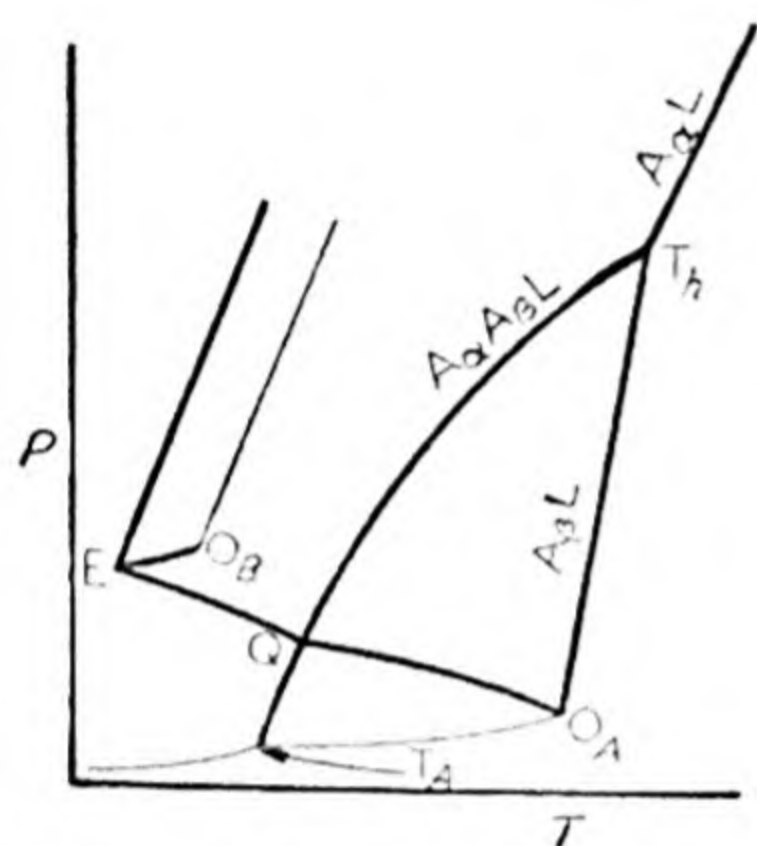


FIG. 6-14. Variation of Fig. 6-6, with high pressure triple point T_h for A.

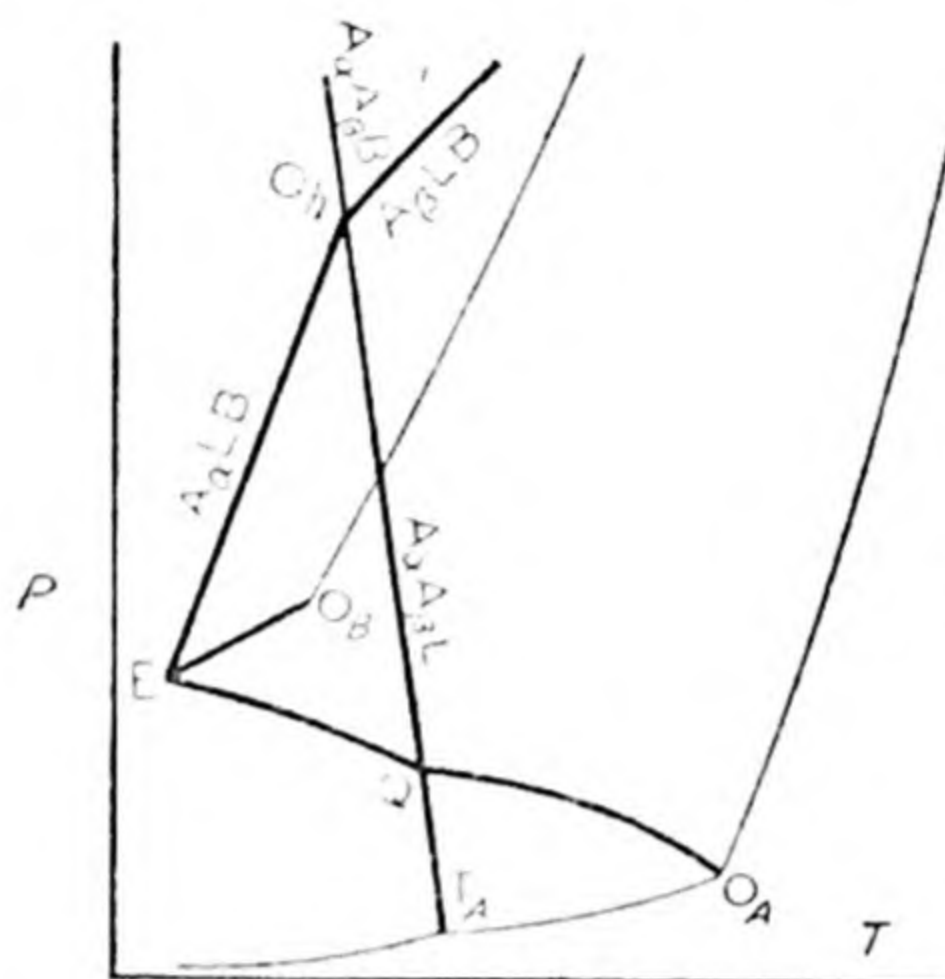


FIG. 6-15. High pressure quadruple point Q_h , for $A_\alpha A_\beta L B$.

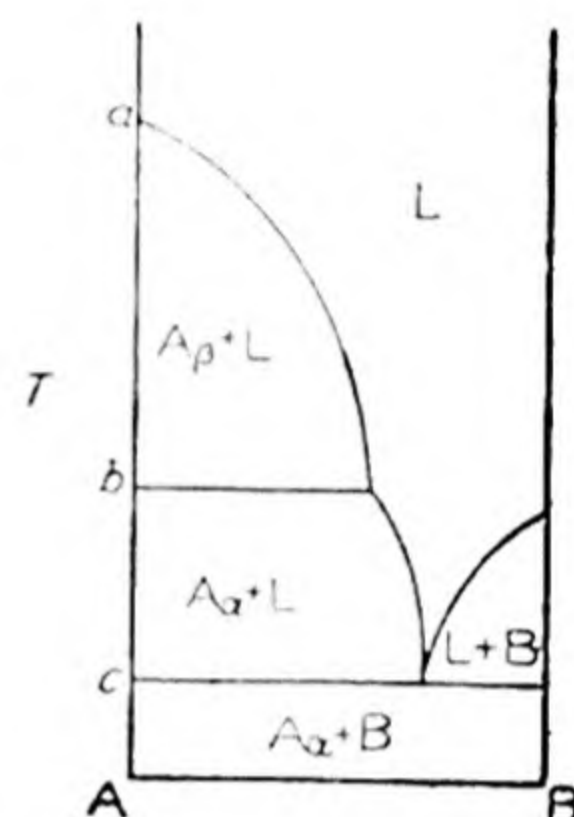


FIG. 6-16. Isobar of Fig. 6-15 just above O_B .

ant T_h , at high pressure, where the transition curve intersects the fusion curve. In this case the solubility surface for the form A_β , or the liquid solution in equilibrium with A_β , is the 3-sided curved surface bounded by the points O_A , Q, T_h ; and the binary vapor in equilibrium with A_β is a surface bounded by the points O_A , Q, T_A .

On the other hand, the $A_\alpha A_\beta$ curve may follow such a course as to intersect, in P/T projection, the "eutectic curve" ALB, at the point Q_h (Fig. 6-15). This will be a high pressure quadruple invariant point involving the phases $A_\alpha A_\beta L B$, the intersection of the following four 3-phase equilibria: $A_\alpha A_\beta L$ from Q, and $A_\alpha A_\beta B$ above Q_h , both of these being coincident in projection with the unary transition curve $A_\alpha A_\beta$; $A_\alpha L B$ from E, and $A_\beta L B$ originating at Q_h . Fig. 6-16 is an isobar of Fig. 6-15, just above O_B ; the LV equilibrium is omitted. In the case of Fig. 6-14, the 3-phase tie-line b, for the equilibrium $A_\alpha A_\beta L$, moves up, with increasing P , to disappear at point $a (= T_h$ of Fig. 6-14); in the case of Fig. 6-15, the same tie-line moves down to meet the line c, for the equilibrium $A_\alpha L B$, at Q_h .

2. If the enantiotropic transition point of A is below the eutectic, and if the transition curve $A_\alpha A_\beta$ has a low positive slope (dP/dT), it may give the three intersections shown in the P/T projection of Fig. 6-17. The first, point Q, is the quadruple point $A_\alpha A_\beta V B$, at a temperature just slightly

above that of T_A . The second, Q_h , is a high pressure quadruple point similar to Q_h of Fig. 6-15 and involving the same four phases. The third, T_h , is simply the unary high pressure transition point for the phases A_α , A_β , and L, entirely similar to T_h of Fig. 6-14.

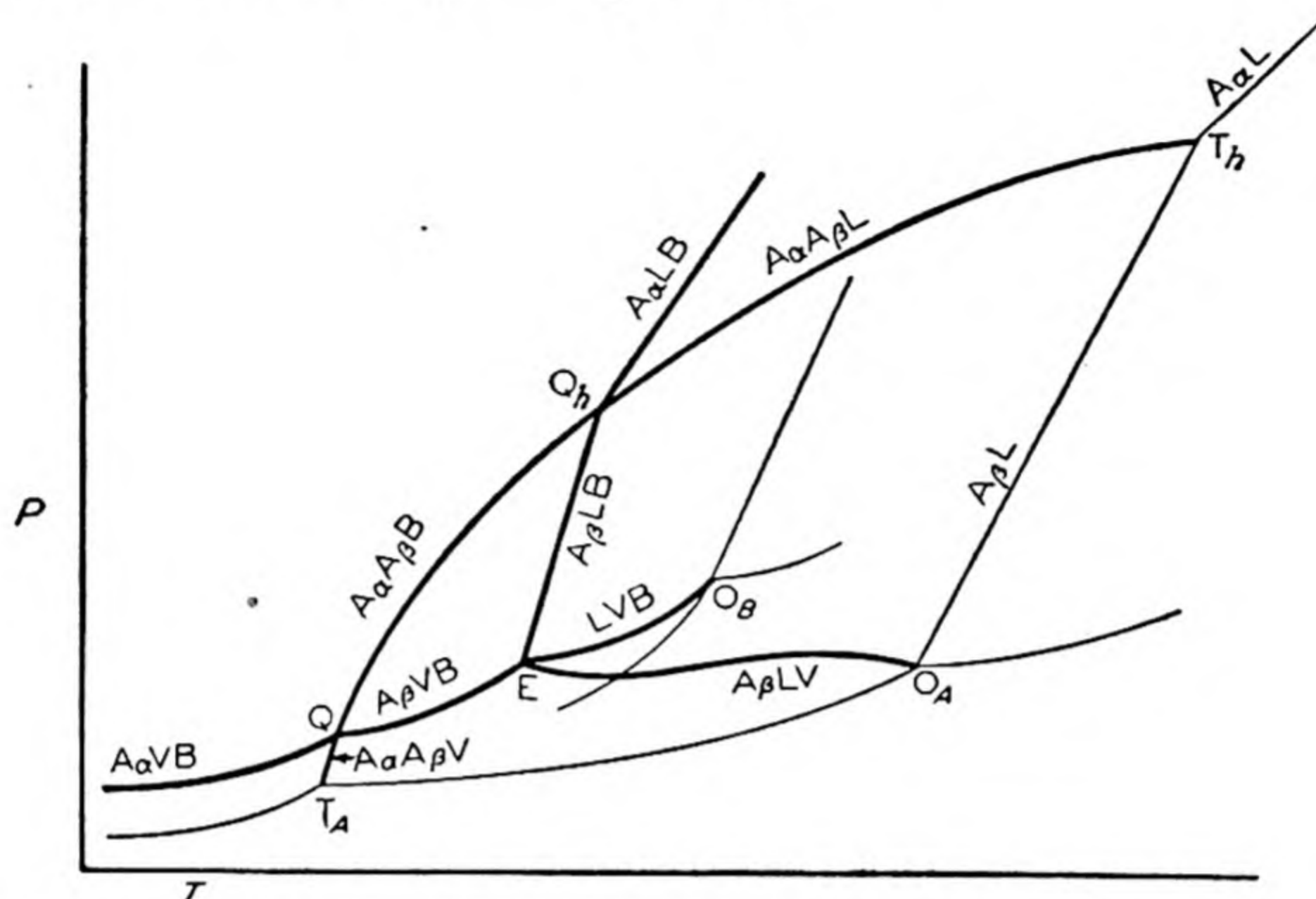


FIG. 6-17. Variation of Fig. 6-15, with Q below E in temperature.

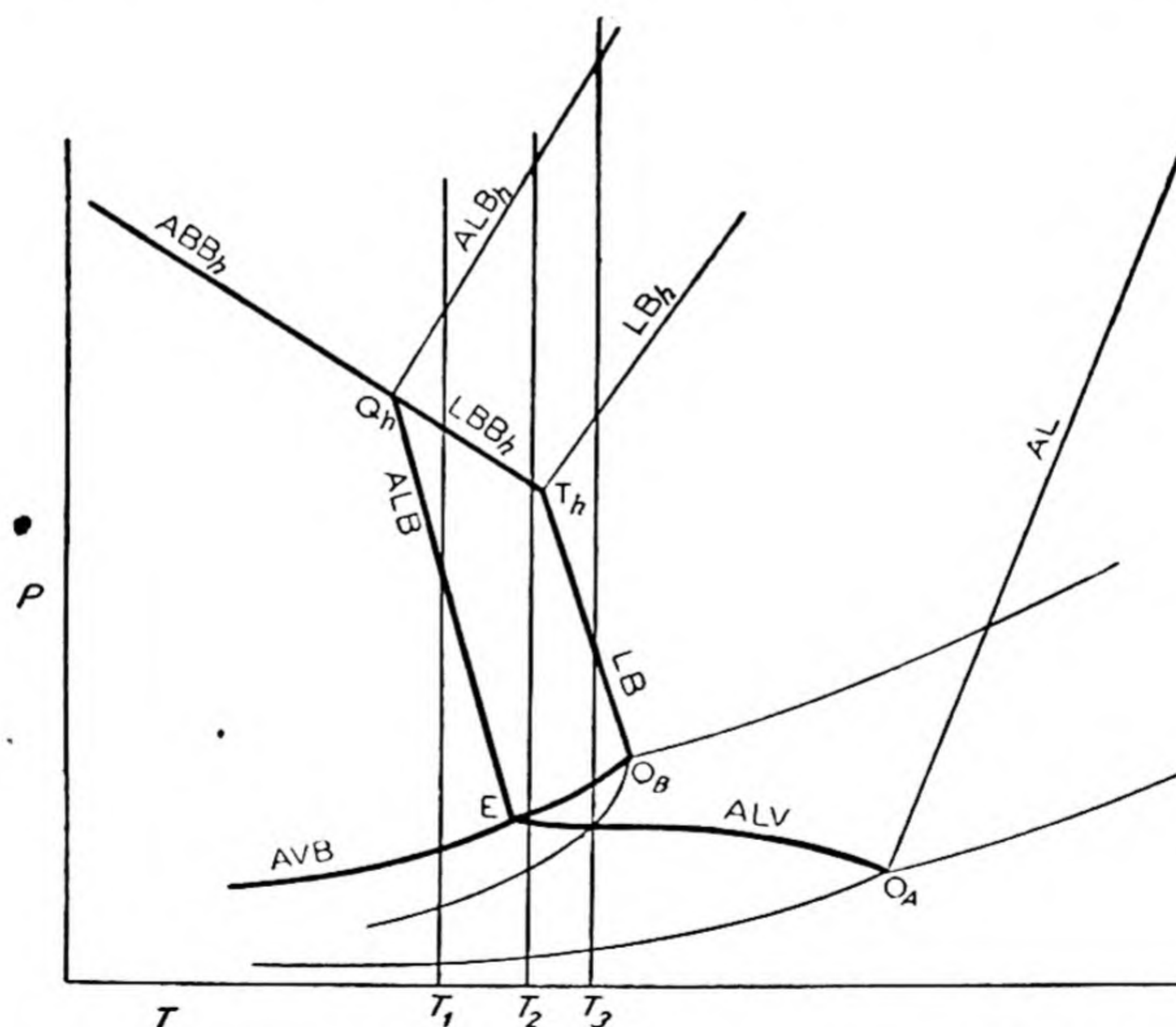


FIG. 6-18. Negative slope of fusion curve for component B (water); B_h is ice III.

3. The type Q_h of high pressure transition point is also to be expected with high pressure polymorphism on the part of a component. In illustration we shall introduce the case in which the fusion curves (S/L) of the components have slopes of opposite sign (Fig. 6-18). The component B may

therefore be taken as representing water with solid forms B and B_h . Again the equilibria ABB_h and LBB_h are coincident, on the projection, with the unary transition curve BB_h . In this case the eutectic curve EQ_h , involving the low pressure form B, may have either a negative or a positive slope, but it must lie on the left of the fusion curve of B, or $O_B T_h$, since at any P the melting point of B is lowered by A if solid B is pure. The curve ALB_h rising from Q_h , however, will have a positive slope since both LB_h and AL are

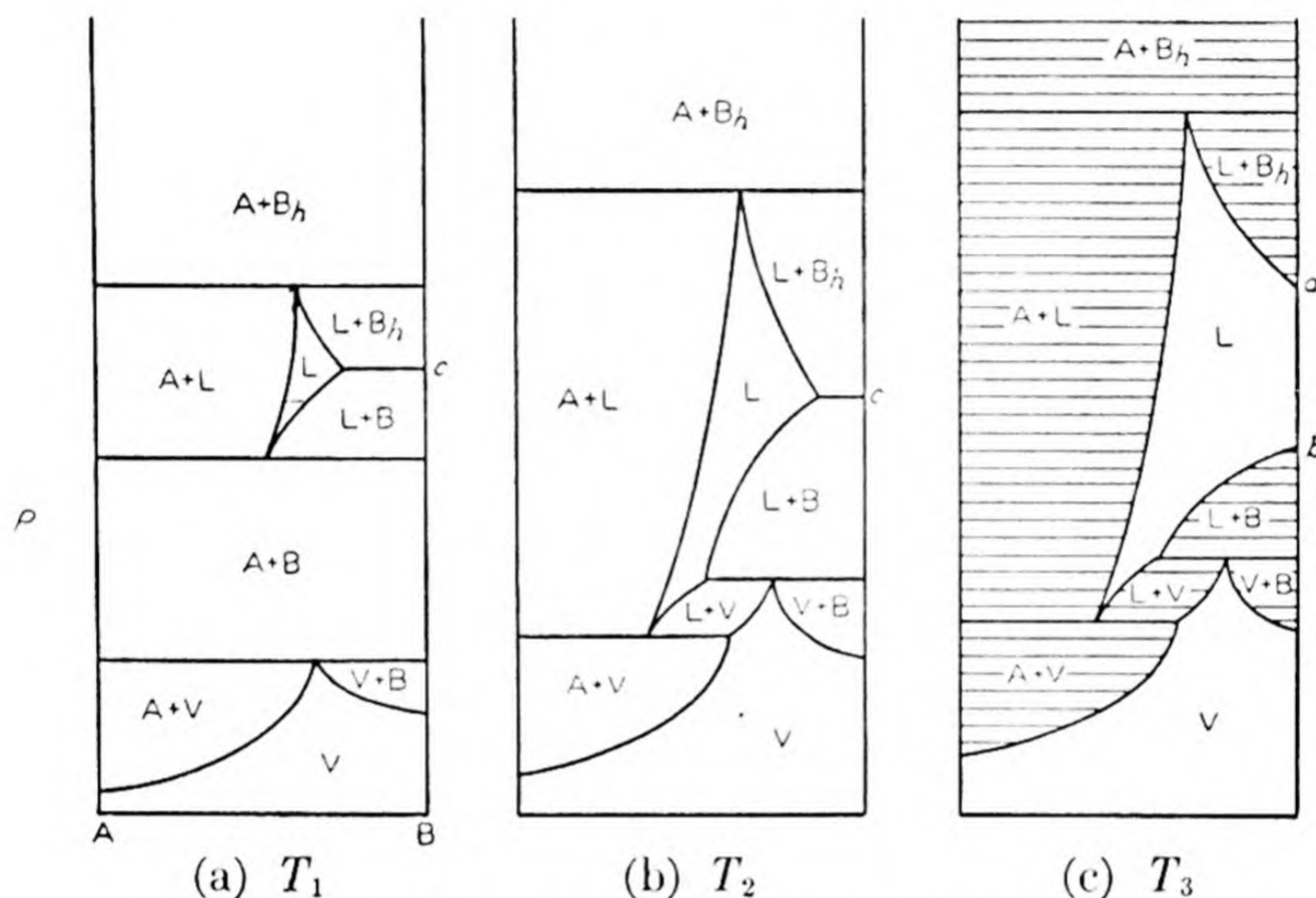


FIG. 6-19. Isotherms of Fig. 6-18.

positive in slope. An isobar between O_B and T_h shows nothing abnormal compared to those given in Chapter V, with all positive slopes. Three isotherms are shown in Fig. 6-19. At T_3 , the component B is seen to have two “melting pressures”: a for the form B_h and b for the lower pressure form B. As T falls below T_3 , these points move together, to merge at T_h , the high pressure transition point of pure B, or the equilibrium LBB_h ; and at lower T the tie-line c appears, for the equilibrium $B + B_h + \text{binary liquid}$. This tie-line is, of course, on the curve $T_h Q_h$ of Fig. 6-18.

F. Pseudobinary Behavior

We shall now suppose that A and B are two substances of the same analytical composition and capable of reversible transformation in a homogeneous phase consisting of $A + B$, hence in the vapor and in the liquid state (since we shall assume them to be completely miscible in the liquid state) and in the solid state if they form solid solution. The nature of the relation between A and B is here of no importance; they may be related as polymers, stereoisomers, positional isomers, optical isomers, etc.

The only condition is that they have the same analytical composition and can attain homogeneous equilibrium in at least one phase. If they are completely soluble as solids, there will be only one possible solid in the system, which may be called S ; this may be variable in composition, variable, that is, in respect to the ratio A/B , and may further have polymorphic forms, S_α , S_β , etc. On the other hand, the solid structures of A and B may be different, and there may be two types of solid solution in the system — S_A based on the structure of A , and S_B on the structure of B . Finally, A and B may be immiscible as solids, and then we shall speak of A_s and B_s , both pure, with possible polymorphism of either.

If A and B attain homogeneous equilibrium *instantaneously* in any homogeneous phase, the combination $A + B$, prepared in any arbitrary proportions, is a unary system, whatever the nature of the solid. The system will have a triple point (SLV) with a temperature and pressure characteristic of the system itself. With the same analytical composition in all three phases at such a triple point the system is unary despite variation in the ratio A/B from phase to phase. In fact it is impossible, in this limiting case, ever to separate the substances A and B , and they are known as tautomeric isomers; it is only as a hypothetical assumption that we here imagined "arbitrary proportions" of the two forms. If the forms are immiscible as solids, then, as we shall see below, under Fig. 6-20, the solid will be either always A or always B .

If, on the other hand, the homogeneous equilibrium is attained with infinite slowness, that is, if the arbitrary or accidental ratio of A to B undergoes no change with time in the range of P and T in which the system is studied, the system is binary.

If the homogeneous equilibrium is attained in finite time, the actual behavior of the system is called **pseudobinary**, a behavior explicable in terms of two limiting types of behavior, the proportion of binary to unary behavior being a function of time or, more generally, of history. The relation is sometimes also called dynamic allotropy or dynamic isomerism, because the pseudocomponents, or the forms A and B , can presumably exist together in homogeneous, reversible equilibrium in some phase.

Fig. 6-20(a) represents a pseudobinary system in which the solid phases are pure A_s and pure B_s ; the continuous curves of this diagram represent the relations of A and B as a binary system, at constant pressure; b_A is the boiling point of liquid A , b_B of B , T_A and T_B their melting points, and E the eutectic. These curves represent the phenomena which would occur if the arbitrary ratio of A and B in any sample remained unchanged with time. The dashed curves, one in the vapor and one in the liquid, give the proportions of A and B (function of T at constant P) for homogeneous equilibrium

in each of these phases. If sufficient time is always allowed (or if a suitable catalyst for the reaction $A \rightleftharpoons B$ is present), the composition of the vapor or of the liquid will always be on these curves. The liquid then, whatever its original ratio A/B , will boil at T_b and will freeze at T_f , and the only solid which would ever appear, if the liquid is not supercooled, is A_s .

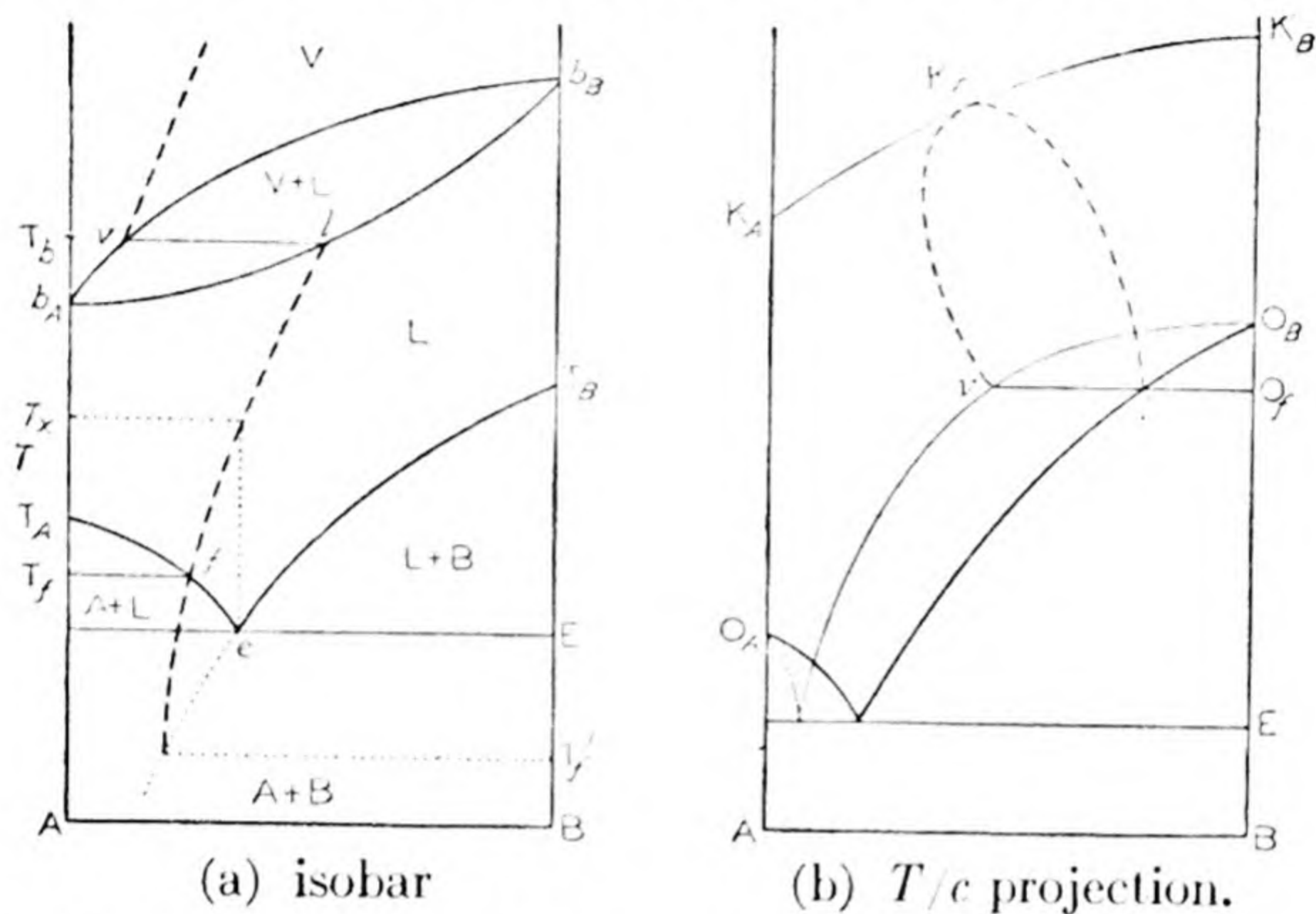


FIG. 6-20. Pseudobinary systems with pure solids.

[The binary diagram, such as T_AeT_B , is determined by studying the relations of A and B without giving the system time for the transformation $A \rightleftharpoons B$; specific inhibitors may sometimes be used. Then the homogeneous equilibrium curve, such as fl for the liquid state, is established by taking a liquid which has been made to come to internal equilibrium (with sufficient time or through the aid of a catalyst), and cooling rapidly to the binary freezing point diagram, whereupon the composition may be determined from the observed freezing point.]

With the L and V phases always in internal, homogeneous equilibrium, the behavior is therefore unary. The points T_b and T_f would be the “natural” constants (normal, at atmospheric P) of the one-component system: T_b the natural boiling point of the liquid, T_f its natural freezing point and the natural melting point of the stable solid A_s . In contrast, the points T_A , T_B , b_A and b_B are known as “ideal” constants.

The actual behavior in finite time, however, depends on the original arbitrary ratio A/B , the original T , and the time; the binary diagram may be said to represent the system in “false equilibrium” relative to its unary behavior. If a liquid in internal equilibrium is rapidly cooled from any temperature above T_x , it will start freezing on the curve T_{Be} , precipitating B_s ; from any temperature below T_x it will produce A_s , but at a freezing point below T_f . Freezing points above T_f , producing A_s , are obtainable only if

the original liquid contains little B and if the transformation $A \rightarrow B$ does not proceed beyond the composition f . A pseudobinary system may therefore form either of two solids, one stable, one unstable, at freezing points varying with the initial T and with the rate of cooling of the liquid.

Solid B will change in time to solid A, at any temperature below T_f , but more rapidly if it is in contact with liquid. At temperatures above T_f it becomes a liquid on the curve fl ; between the temperature of E and T_f it first liquefies and then resolidifies as A_s . Either solid, when heated, will melt at its "ideal melting point," T_A or T_B , the temperatures of the equilibria $A_s + \text{pure liquid A}$, and $B_s + \text{pure liquid B}$, respectively. But these are not stable equilibria, since the liquids are not in homogeneous equilibrium. The only stable melting point is T_f , for $A_s + \text{a liquid of composition } f$. When A_s is heated, it begins to melt at its ideal melting point, T_A , but as the liquid changes in composition, with A transforming into B, the melting point drops to the natural freezing point T_f .

The schematic relations of Fig. 6-20(a) are illustrated by the system α -(anti) benzaldoxime as form A, and β -(syn) benzaldoxime as form B. For this pseudobinary system, $T_A = 34^\circ$, $T_B = 130^\circ$, $E = 25^\circ$, and T_f , with α as the stable solid modification, is at 27.7° . The equilibrium curve for the proportion of α and β in the liquid is practically vertical (independent of T at ordinary P), with about 5% β .¹¹ While Fig. 6-20(a) is assumed to be isobaric, Fig. 6-20(b) represents the T/c projection of such a pseudobinary system, which differs, however, from that of 20(a), in that the stable solid is B rather than A. The relations of Fig. 6-20(b) may be taken as schematic for the pseudobinary system acetaldehyde (A)–paraldehyde (B), with the following constants, the compositions being in mole percent:¹²

Ideal Constants ($^\circ\text{C}$)		Natural Constants	
		$T(^\circ\text{C})$	% B
$K_A \dots 188$	$K_B \dots 290$	$K_f \dots 218$	11
$b_A \dots 21$	$b_B \dots 124$	$T_b \dots 42$	53 in L 1.5 in V
$T_A \dots -118$	$T_B \dots 12.5$	$T_f \dots 6.75$	88 in L
$E \dots -120(1.4\% \text{ B})$			

In the case of sulfur the variety of molecular species other than the rings of eight sulfur atoms required for the crystallization of the pure enantiotropic forms (rhombic and monoclinic) may be grouped, for simplicity, as a second component (B), and the variability of the melting points may then

¹¹ F. K. Cameron, *J. Phys. Chem.*, **2**, 409 (1898).

¹² R. Hollmann, *Z. phys. Chem.*, **43**, 129 (1903). According to A. Smits and H. L. de Leeuw, *ibid.*, **77**, 269 (1911), however, metaldehyde, or $(\text{CH}_3\text{CHO})_4$, must also be considered, in addition to paraldehyde, or $(\text{CH}_3\text{CHO})_3$, making the system pseudoternary.

be explained on the basis of pseudobinary behavior. In Fig. 6-21,¹³ T_M is the ideal melting point of the monoclinic, T_R that of the rhombic variety; T_{Mf} and T_{Rf} their respective natural freezing points. If rhombic sulfur is heated rapidly, above its enantiotropic transition point 96° , it begins to melt at its ideal melting point (T_R , 113°) to a liquid which is presumably pure A (8-membered rings of sulfur atoms¹⁴). As this liquid becomes complex in constitution (whatever the explanation¹⁵), its composition in respect to the new groups of species, here called B, moves toward the equilibrium position defined by the dashed curve of the figure, at the given P and T ; hence the melting point drops to the natural one at T_{Rf} (110°). Both T_R and T_{Rf} , however, are metastable in respect to the higher enantiotropic form, monoclinic sulfur. During the process just discussed, then, there is the chance of the solidification of the whole mass to monoclinic sulfur. This solid, heated by itself, begins to melt at T_M (119°), its ideal melting point, but the temperature is not constant, as the liquid becomes binary, until the equilibrium concentration is reached, giving the natural freezing point T_{Mf} at 114.5° . This is the only stable freezing point of sulfur. Since, moreover, the equilibrium of the forms in the liquid state is not at all rapidly attained, and since the equilibrium curve moves considerably toward B at higher temperatures, a great variety of effects will be possible, including supercooling and resulting vitreous and plastic conditions.

Monotropy (according to Smits¹⁶). If the liquid in Fig. 6-20(a), while still always in homogeneous equilibrium, is supercooled through T_{Ae} , the freezing point curve of A_s , it may, on reaching the metastable extension of the freezing point curve of B_s , precipitate B_s at the temperature T'_{fj} . Solid B_s may now be considered as an unstable, monotropic form; it can never be in stable equilibrium with A_s and vapor. The temperature T'_{fj} , as shown in Fig. 6-22, is the (normal) melting point of the monotropic form (cf. Fig. 2-15).

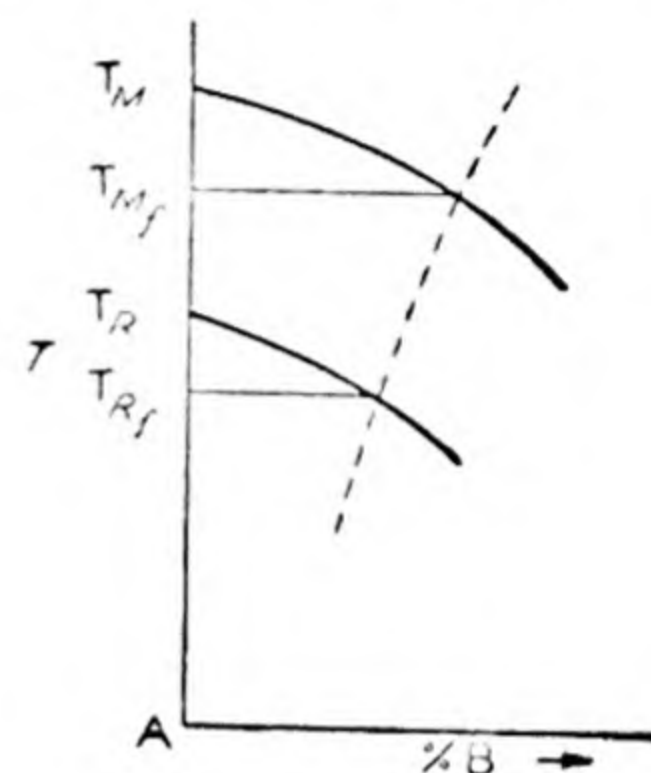


FIG. 6-21. Pseudobinary behavior of sulfur.

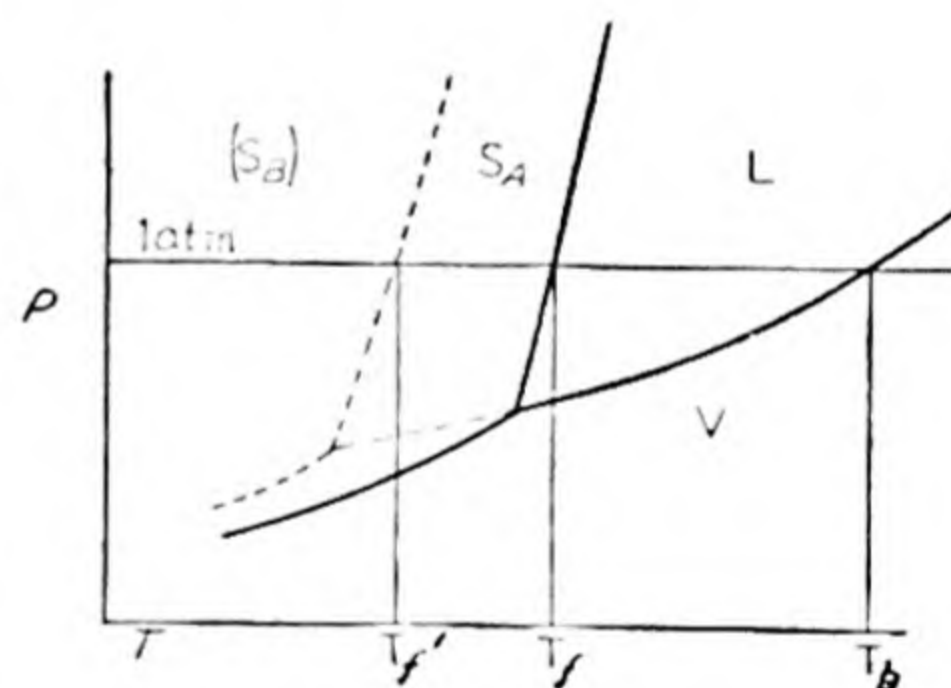


FIG. 6-22. Monotropy.

¹³ A. Smith and C. M. Carson, *Z. phys. Chem.*, **77**, 661 (1911).

¹⁴ B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935).

¹⁵ As in terms of the opening and polymerization of the chains of sulfur atoms: R. H. Ewell and H. Eyring, *ibid.*, **5**, 726 (1937).

¹⁶ A. Smits; the books mentioned under Ref. R.

Again, if the homogeneous equilibrium is instantaneously attained in the liquid state, the system would be a unary system with monotropy, and the normal constants (that is, at atmospheric P) would be: T_f , the melting point of the stable form, here interpreted as A_s ; T'_f , that of the monotropic form, here B_s ; and T_b , the boiling point of the liquid.

Whether or not, even in this interpretation, this monotropic form may become stable at high P is still a question, as discussed in connection with Fig. 2-12. As P increases, the temperature and composition (ratio A/B) of the binary eutectic diagram (Fig. 6-20(a)) may be supposed to change in quantitative relations. At the same time there will be some shifting of the internal equilibrium curve of the liquid. If, as a result of both these effects, the internal equilibrium curve moves toward the eutectic, then at the pressure where it reaches it the liquid can exist in natural or stable equilibrium with either solid form. This will be a high pressure transition point, at which B_s , monotropic at low P , becomes a stable polymorphic form at high P ; and above this particular pressure the homogeneous equilibrium curve would cut the T_{Be} curve, so that the natural freezing point would involve B_s (but at high P).

If the freezing points are variable, depending on the history of the liquid, then the system is not only monotropic but also pseudobinary. If, finally, the melting points are also variable, that is, the temperatures at which a solid first begins to melt, then the solids are no longer pure forms but their solid solutions. On this basis the behavior of phosphorus in respect to the relations of the white and red forms may be explained, as in Fig. 6-23, again on the assumption that only two forms are involved.¹⁷ (If the complexity is great it becomes necessary to assume pseudoternary or even higher order behavior.)

It is assumed in this diagram that the pseudocomponents, A and B , form two types of solid solution — S_A based on A (white phosphorus, S_w), and S_B based on B (red phosphorus, S_R), in a eutectic system.¹⁸ The diagram is the projection, on the T/c plane, of equilibria involving the vapor phase. (If the vapor curves are erased, it therefore becomes the diagram of the "condensed system," but this would not mean an open air system since the vapor pressures are greater than atmospheric.) It is also assumed that the svl equilibrium proceeding from T_A extends metastably below the eutectic, as shown by the curves from T_A to the points s_m , v_m , l_m . A system consisting of liquid and vapor, in internal equilibrium with respect to the pseudocomponents, has the compositions given by the homogeneous equilibrium curves v_RK and Kl_R , which are also shown extended as the

¹⁷ A. Smits and S. C. Bokhorst, *Z. phys. Chem.*, **91**, 249 (1916).

¹⁸ The diagram may also be peritectic in type, as discussed in Ref. (17).

dotted curves $v_R v_w$ and $l_R l_w$ for the supercooled state of the LV system. K is therefore the natural critical point of the substance.

If a liquid is cooled to the liquidus T_{BE} it should, if not supercooled, precipitate S_B , or red phosphorus, with composition on the solidus bT_B , and the sample will show, in general, a freezing point range, as usual. If, however, the LV system is in internal equilibrium with respect to proportions

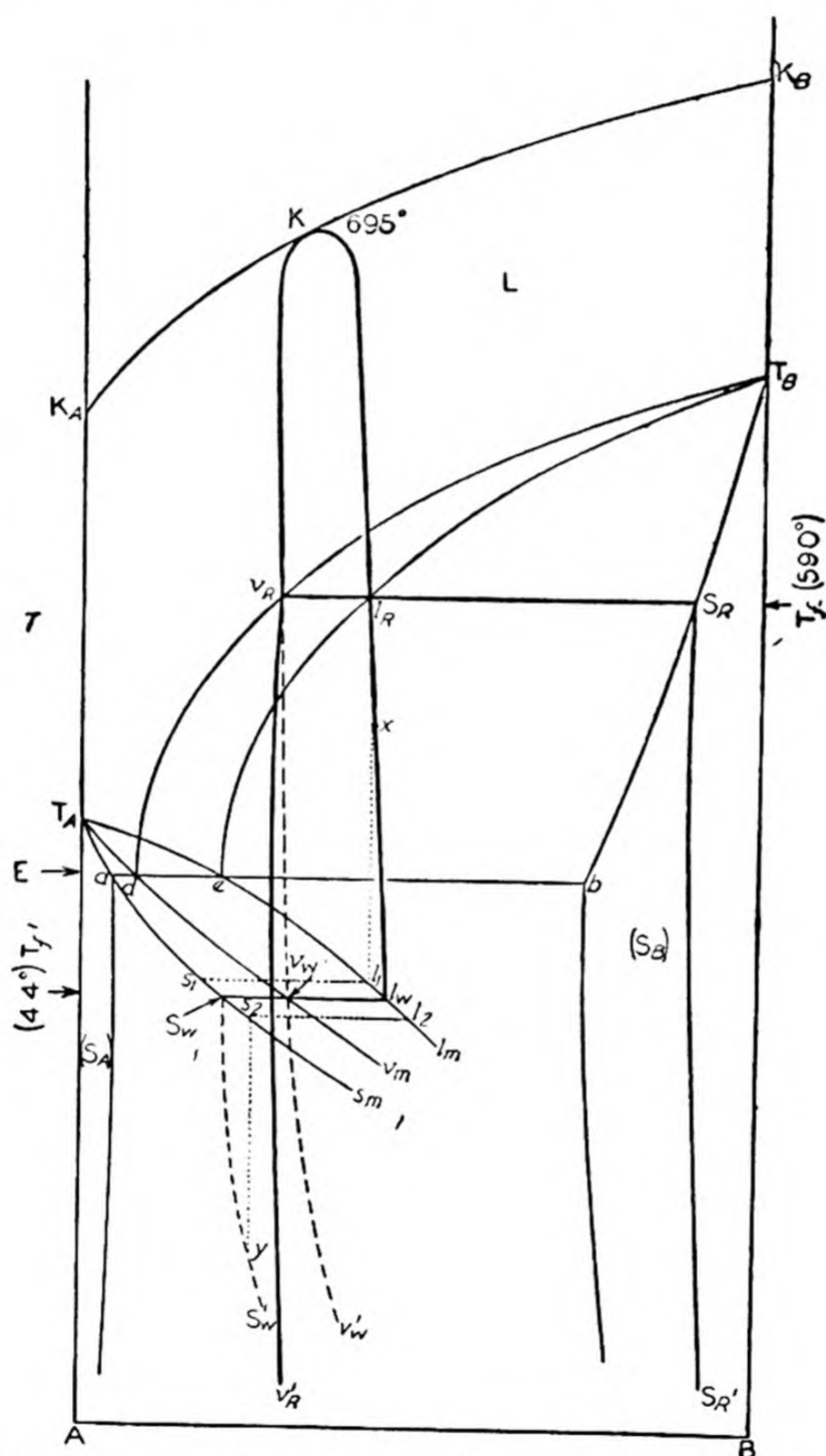


FIG. 6-23. Phosphorus as pseudobinary (according to Smits).

of the pseudocomponents A and B, so that it lies on the curve just mentioned, $v_R K l_R$, and if this internal equilibrium is maintained during the freezing, the sample will freeze at constant temperature, at the natural freezing point T_f , the triple point $v_R l_R S_R$. If the resulting SV system is cooled, its properties, depending upon its constitution or the proportion of A and B forms in it, will vary with its treatment. The equilibrium con-

stitution is represented by the curves $v_R v'_R$ and $S_R S'_R$. Upon heating, the melting point will be T_f only if the SV system is in such internal equilibrium; the melting point is otherwise higher or lower, and variable during melting.

If the LV system, while in internal equilibrium, is supercooled through the liquidus and vaporus curves eT_B and dT_B , it may reach the metastable extension of the melting curves of the S_A form, at points v_w and l_w . Here S_w (white phosphorus) solidifies, and if the internal equilibrium is maintained during the process, the point is an invariant, triple point, $S_w v_w l_w$, the (metastable) natural freezing point for white phosphorus, T'_f . But if the liquid is suddenly cooled from some point such as x , without maintaining internal equilibrium, the freezing point would be higher ($s_1 l_1$) and the solid would have different properties. Similarly, the curves $S_w S'_w$ and $v_w v'_w$ are the curves of internal equilibrium for the system SV of white phosphorus. If a solid in internal equilibrium is suddenly heated, as from point y , it will melt below T'_f , at $s_2 l_2$.

The monotropic, unary diagram of Fig. 2-16 may now be related to Fig. 6-23. In 2-16, the substance phosphorus is assumed to be always in internal homogeneous equilibrium with respect to its pseudocomponents. The composition variable therefore vanishes, and in the P/T diagram the co-existing phases are superimposed. Point O is T_f , while T_β is T'_f .

Chapter VII Binary Compounds

A. Phase Rule Concept of Binary Compound

A binary compound C, from the point of view of the Phase Rule, is a substance known to be formed reversibly in phase reactions by the combination of two other substances, and with a composition, in respect to these substances, constant and independent of P and T . We assume that A and C and C and B, like A and B themselves, form a single liquid phase, but that as solids A and C, or C and B, may be either completely or incompletely miscible, or entirely immiscible.

If a compound of A and B is completely stable, or completely undissociated into A and B in every state (S, L, V), even through a critical point, then it is not a binary compound in the Phase Rule sense just defined. It is merely a third substance, the plane of its composition lying parallel between those of A and B throughout the P, T, c model, and giving rise to two independent binary systems, A-C and C-B. The Phase Rule study of these systems would then reveal nothing to suggest any relation in composition between C and either A or B. All the equilibrium phase relations of a complex of the composition C (that is, of A and B in the proportion C) would involve phases of identical composition, with no binary behavior whatever. This identity of the compositions of the phases during transition is, unlike that of the azeotropic maximum or minimum discussed in Chapter III, independent of P and T . If the composition of the phases at such points of identity of composition is independent of P and T , the transition will be called **congruent**. If all the phase transitions of the complex C, then, are congruent, it is not recognized as a binary compound but as an independent substance. In congruent transition, the substance undergoes 2-phase transition ($S \rightleftharpoons L$, $S \rightleftharpoons V$, $L \rightleftharpoons V$) isobarically at constant T , independent of the proportions of the phases or of the "transition ratio." A binary compound may or may not undergo some congruent transition, in some range of P and T , but it will always show some kind of **incongruent** transition, which is merely another way of saying that it will decompose in some phase reaction or, in reverse, that it will be observed to be formed from the components in some phase reaction. This means that its limits, in P and T , of stability with respect to A and B will be such as to cause, at least before its critical

point can be reached, some phase reaction of decomposition or an incongruent transition.

But as pointed out in Chapter I in connection with the vaporization of NH_4Cl , unary behavior (complete congruence of all transitions) does not necessarily prove that we are dealing with a single species. If there is homogeneous equilibrium in every phase with respect to the reaction $\text{A} + \text{B} \rightleftharpoons \text{C}$, the phases in transition equilibrium may have the same analytical composition, expressed in terms of A and B, but may vary in the proportions of the actual species A, B, and C, the system still remaining unary in behavior. This at least would hold true if the species A and B have

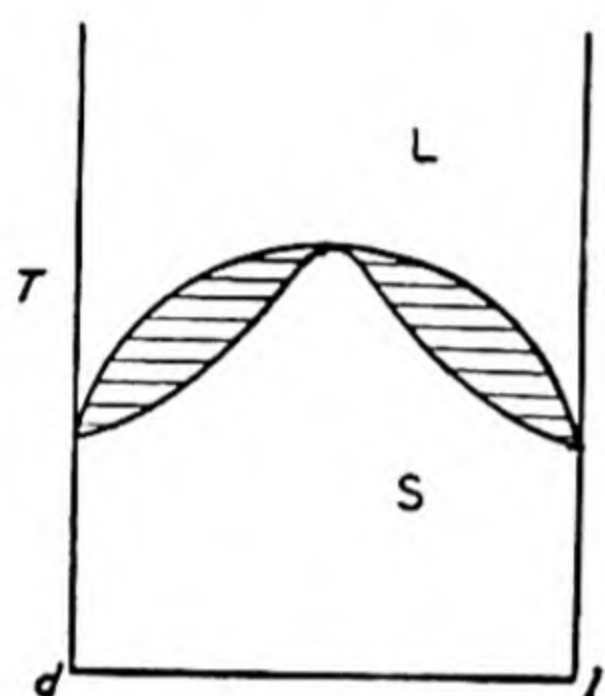


FIG. 7-1.
Carvoxime.

the same solubilities throughout; thus as an extreme case we may consider the melting point curve of the optical isomers of carvoxime (Fig. 7-1), a rare case of continuous solid solution with maximum melting point.¹ Although a definite compound is suggested by the diagram, it must be realized that the maximum, and hence the identity of composition of the two phases, must be at the unimolecular ratio and furthermore independent of P , because of the necessary symmetry of the system. In fact the 1:1 solid solution must show a unary triple point, an invariant equilibrium of constant P and T

involving three phases, S, L, V, all of the same composition, regardless of the degree of dissociation of the supposed compound in any state.

The contact of the two curves (*Ph 1* and *Ph 2*) of a continuous phase transition, such as Fig. 7-1, is expected to occur only at a maximum or a minimum, and then a compound is indicated if the composition of the point of contact is independent of P and T . A contact at an intermediate point is sometimes reported: at the ratio 1:1 in the melting point curves of the systems bromine-iodine² and magnesium-cadmium,³ both forming continuous solid solution; and at the 1:1 ratio in the $(P/c)_T$ liquid-vapor curve of water-acetic anhydride.⁴ It seems, however, that if these are true points of contact with compositions independent of P and T , a compound stable in both states would be indicated; but then the contact would not be a tangential one between smooth curves. If the two curves (*Ph 1* and *Ph 2*) have no breaks from pure A to pure B as the components of the system, their contact can be only at a maximum or a minimum.⁵ The Mg-Cd diagram as

¹ J. H. Adriani, *Z. phys. Chem.*, **33**, 453 (1900).

² P. C. E. M. Terwogt, *Z. anorg. Chem.*, **47**, 203 (1905).

³ G. Grube, *ibid.*, **49**, 72 (1906).

⁴ K. P. Miscenko and S. J. Tscherbou, *Z. phys. Chem.*, **A-148**, 386 (1930).

⁵ On the corresponding question for ternary systems, see R. V. Mertzlin, *Bull. acad. sci., U.R.S.S., Sér. chim.*, 1937, p. 1407.

given by Hume-Rothery ⁶ in fact does not show the contact of solidus and liquidus, although there is a maximum in the underlying continuous solid-solid transition, of the type of point *m* in Fig. 6-5(e).⁷ The maximum occurs at the ratio 1:1 and indicates, if not a definite compound, at least a "superlattice" or a region of organization of the crystal not based on the structure of the individual metals.

In any case if a transition such as $L \rightleftharpoons V$ or $S \rightleftharpoons V$ proves to be congruent (the composition of the congruent phases being independent of *P* and *T*, and the transition proceeding, at arbitrary *P*, at a constant *T* independent of the ratio of transition), the question of the actual existence of the compound in the vapor phase, for example (or in *Ph* 2 in general), requires information other than that of the phase diagram, a necessity pointed out in connection with Fig. 7-1. The property most commonly studied, in the case of the vapor phase, is the density. Thus the density of the vapor of ammonium chloride gives the extent of formation, if any, of the compound as compared to the substances NH_3 and HCl ; similarly for the extent of decomposition of the vapor of "sulfuric acid," or the vapor in equilibrium with any of the binary compounds in the system $\text{SO}_3\text{-H}_2\text{O}$, all of which we may formulate additively. But an interesting point arises in connection with a "mono-hydroxy acid." If the densities of these vapors of binary compounds are studied as $f(P, T)$, the variation may be interpreted either as a variation in the reaction $A + B \rightleftharpoons A \cdot B$ or as a variation in the reaction $A \cdot B \rightleftharpoons 2[(A \cdot B)_{\frac{1}{2}}]$. The 1:1 compound in the system $\text{H}_2\text{O-Ac}_2\text{O}$ (acetic anhydride), called acetic acid, gives a vapor with density falling from the sum of the densities of H_2O and Ac_2O to their average, as *T* is increased or as *P* is decreased; and this is interpreted as the breaking down of a dimer of CH_3COOH into the monomer. But such densities are also consistent with a 1:1 compound of H_2O and Ac_2O merely dissociating into its components H_2O and Ac_2O . A vapor density of 60 ($\text{O}_2 = 32$) for the vapor of "acetic acid" at low *P* may mean an actual molecular weight of 60, with particles of the composition CH_3COOH , but it may also mean a 1:1 mixture of two kinds of particles of different molecular weights, H_2O and Ac_2O . This ambiguity in the interpretation of the vapor density exists for any so-called mono-hydroxy acid, the vapor density as the monomer (HNO_3 , for example) being the average of those of water and the anhydride. Since it is not certain that the ambiguity can, in general, be resolved by chemical methods, it would seem to be necessary to resort to diffusion experiments

⁶ W. Hume-Rothery, *The Structure of Metals and Alloys*, Institute of Metals, London, 1945; p. 76.

⁷ Hansen's diagram (*loc. cit.*, p. 431) also shows this maximum, but the solid solution is presented as discontinuous at the actual melting point curve.

or to mass-spectrography. "Structural analysis" through X-ray or electron diffraction is in this respect inconclusive, if it itself is dependent on knowledge of the actual molecular weight and composition of the particles or molecules of the gas, the very point which may not be settled by the density data.

The question, then, of the extent of the homogeneous reaction $A + B \rightleftharpoons C$ is one which has only an indirect bearing on a phase diagram. It is possible, for example, to analyze the isobaric solubility curve of a pure solid binary compound by making a number of assumptions, in such a way as to estimate its degree of dissociation (x) in the liquid phase, at its observed melting point, essentially from the flatness of its melting point curve. For this purpose, the values of certain quantities such as (1) x , (2) K , the equilibrium constant of the reaction $A + B \rightleftharpoons C$ in the liquid, (3) ΔH , the heat of fusion of the compound (both of these being assumed independent of T), and (4) T_0 , the melting point of the compound if there were no dissociation in the liquid — are adjusted, by trial and error, until a curve can be calculated to match the observed curve.⁸

But the very existence of the compound in the second state (the liquid, on melting, for example) is entirely a secondary question in the Phase Rule. We consequently expect to deal equally with a compound which may be considerably stable in the liquid or vapor state and with one which may have no significance except in the solid state. Even a congruently melting compound, such as $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, may have no existence as such at all in the liquid state. The properties of the solution, for example, even at the temperature of the melting point of the compound, may vary in such a way with respect to composition as to show no evidence of the individuality of this particular ratio of the components. Such compounds are sometimes called "phase rule compounds," implying that their existence is limited to the solid state. While $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is called a "phase rule compound," " H_2SO_4 " or $\text{SO}_3 \cdot \text{H}_2\text{O}$ is customarily called a real chemical compound, one with molecular individuality, in other words. But the information for this distinction does not come from the phase diagram. Indeed the variation of the properties of the liquid $\text{SO}_3\text{--H}_2\text{O}$ (that is, from pure H_2O to pure SO_3) with respect to composition bears surprisingly little relation to the sequence of solid compounds obtainable from it by freezing, including the "real" compound, " H_2SO_4 ." ⁹

⁸ R. Kremann, *Monatsh.*, **25**, 1215 (1904); *Z. Electrochem.*, **12**, 259 (1906). For applications, see J. Kendall and J. E. Booge, *J. Chem. Soc.*, **127**, 1768 (1925); J. D. M. Ross and I. C. Somerville, *ibid.*, 1926, p. 2770; C. M. Bennett and R. L. Wain, *ibid.*, 1936, p. 1114.

⁹ See the graph prepared by R. Knietzsch, *Berichte*, **34**, 4069 (1901), p. 4087; the graph is also given in F. Ephraim, *Inorganic Chemistry* (P. C. L. Thorne and A. M. Ward), Gurney and Jackson, London, Fourth Revised Edition, 1943, p. 573. See also the system pyridine-acetic acid, S. Venkataraman, *J. Indian Chem. Soc.*, **17**, 297 (1940).

It is accordingly altogether more proper, from the strict point of view of the phase diagram, not to introduce distinctions in the formulation of binary compounds, but to write them all in the fashion of "addition compounds," or "hydrates," in the case of binary compounds in aqueous systems. Since " H_2SO_4 " does not have a triple point comparable to that of water, then as a compound in the system $\text{SO}_3\text{--H}_2\text{O}$ it is not different, except in degree, from $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in the system $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$; or since " $\text{Ca}(\text{OH})_2$ " does not vaporize congruently, it is not different from $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. The formulas H_2SO_4 , $\text{Ca}(\text{OH})_2$, NaOH , CH_3COOH , CaCO_3 , NH_4Cl , in other words, rather than $\text{SO}_3 \cdot \text{H}_2\text{O}$, $\text{CaO} \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{O} \cdot \text{H}_2\text{O}$, $\text{Ac}_2\text{O} \cdot \text{H}_2\text{O}$, $\text{CaO} \cdot \text{CO}_2$, $\text{NH}_3 \cdot \text{HCl}$, represent the reactions and properties of these compounds in other connections, usually their reactions not as actual phases but as part of an aqueous solution; or they may be based on structural analysis. But they fail to suggest their actual phase behavior, and they imply what may be non-existent qualitative differences between them and so-called addition compounds. The vaporization of the solid "acid" H_2SO_4 may be congruent, whereas that of the "base" $\text{Ca}(\text{OH})_2$ or the "hydrate" $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is incongruent; but this may be merely the result of the difference in the volatility of the decomposition product SO_3 as compared with CaO or CaCl_2 . When we come to the vaporization of liquid " H_2SO_4 " the incongruence is similar to that of the solution of alcohol and water on either side of the azeotropic composition.¹⁰

It also follows that the mere existence or non-existence of compounds, whether congruently or incongruently melting, on the freezing point diagram of a system, may not be used to deduce the degree or type of "interaction" between the components in the liquid state. Such information can be derived only from the shape and slope of freezing point curves, or their deviation from ideality; and this information may indicate as strong a "molecular interaction" in the liquid state, without solid compound formation, as in cases in which such solid phases appear.

Whether or not the compound melts congruently at a given P appears to depend on its melting point (in relation to the melting points of the components), and this in turn, we may say, on its specific stability. Fig. 7-2

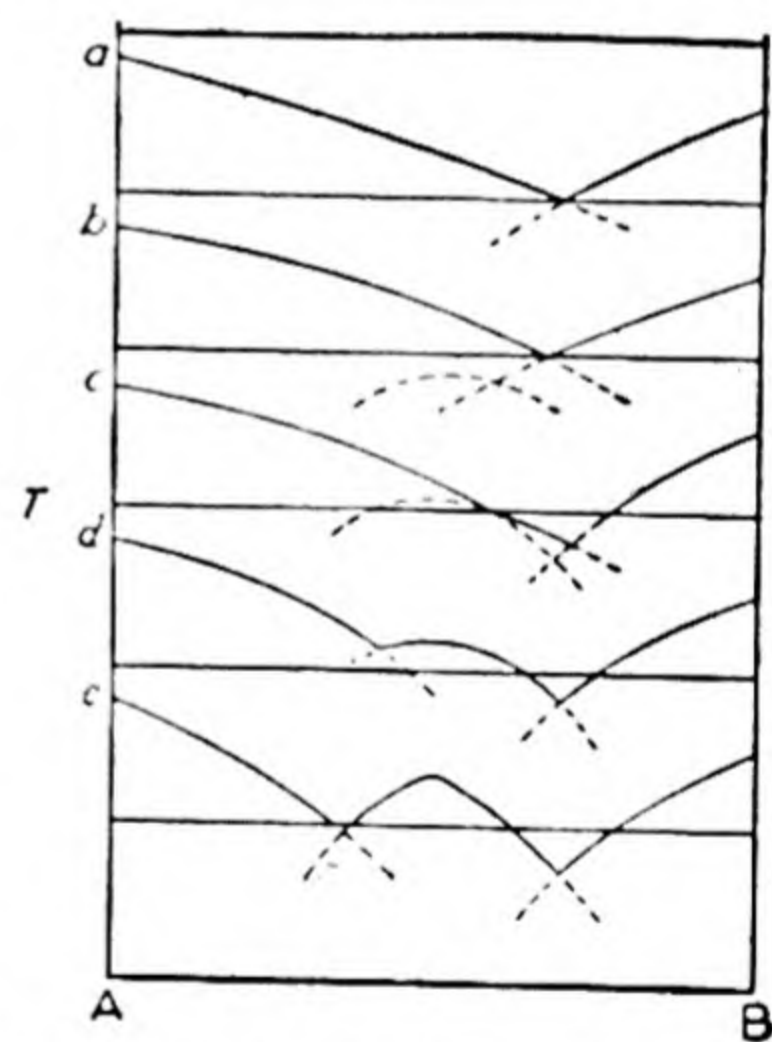


FIG. 7-2. Effect of stability of compound on phase diagram.

¹⁰ "Sodium hydroxide" is written NaOH as though it consisted simply of the ions Na^+ and OH^- . Yet the electrolysis of "anhydrous" molten NaOH yields hydrogen at the cathode as from any *other* aqueous solution of a sodium compound, here Na_2O .

(from Kendall, Davidson and Adler ¹¹) represents, in the order (a) to (e), the increasing tendency on the part of the components to form a compound, or the increasing stability of the compound; it is assumed, of course, that the systems are otherwise identical (if this is ever possible) and at the same P . Two kinds of difference are to be noticed, as we proceed from (a) to (e). As the "compound forming tendency" increases, then, if this means negative deviation from ideality, the freezing point curves of case (a) should be ideal, and they should become steeper and steeper as we go from (a) to (e). At the same time the melting point of the compound rises. In (b) it is altogether "submerged" or metastable; in (c) it is incongruently melting, its melting point being metastable; in (d) it is congruently melting, but with a very flat maximum indicating high dissociation; and in (e) it has marked stability, with a sharp maximum. In (d) and (e) the compound is said to possess an "open maximum."

But the relation between the actual or observed melting point of such an additive binary compound and the "interaction tendency" of the components A and B in the liquid state is not simple. The presence or absence of a solid compound in a melting point diagram may involve questions of crystallographic requirements of the possible solid, and not necessarily the degree of interaction of the components in the solution. Especially if the "interaction" in different systems is to be compared, it is the degree of non-ideality of the melting point curves rather than the presence or absence of solid compounds that is to be used. If the liquid of the system of case (e), for example, should be supercooled to give the metastable simple eutectic system, the freezing point curves of pure A and pure B would presumably be considerably non-ideal; and if such a non-ideal eutectic system fails to precipitate the solid compound, there is no way in which we could prove that it is or is not metastable, and hence no way of knowing whether or not such a compound "exists."

Fig. 7-2 may also be taken to represent the effect of variation in P on the system, so that a compound may appear or disappear, or change from congruently melting to incongruently melting, as a result of change in P (cf. Fig. 7-6).

The "melting" or "vaporization" of a binary compound then may be inherently a complete dissociation, even if it is a congruent process of transition; this is possible with " NH_4Cl " or " $(\text{NH}_4)_2\text{S}$." The formation of these compounds in phase transitions does not imply necessarily the existence of a molecular species of that composition, in any sense. They may represent merely certain structures in organized or anisotropic states (crystalline or

¹¹ J. Kendall, A. W. Davidson and H. Adler, *J. Am. Chem. Soc.*, **43**, 1481 (1921).

liquid crystalline). This point is connected with the question of the proportions of A and B to be expected in such compounds. In dealing with a molecular species of two elements, not only do we expect stoichiometric (integral atomic) proportions of A and B in the compound in the usual sense, but even aside from all valence rules the size of the molecule (the number of atoms it is to contain, let us say) limits the possible number of integral proportions for the "binary" compound. But if the size of the "molecule" is infinite or at least extremely large, as in a crystal or in a mesomorphic state, this limitation, as to the number of integral relations, and with it the very necessity of any integral relations, may disappear; the requirements of crystalline stability may or may not be satisfied with ordinary stoichiometric proportions. The great majority of the binary compounds (daltonides) do preserve integral relations, but in a few cases (berthollides) it appears that the factors of size and geometry may predominate to such an extent as to require non-integral proportions. This is taken as the explanation of the "non-stoichiometric compounds" $\text{Fe}_5\text{S}_{5.55}$, $\text{Ni}_1\text{O}_{1.005}$, etc.¹² These compounds, stable apparently only when deficient in respect to the metal (always, however, one of variable valence), may be considered analytically as solid solutions of the higher valence compound in the lower. Structurally, however, it seems that they are not additive or substitutional solid solutions but "subtractive solid solutions,"¹³ characterized by lattice deficiencies. But this again, like that of the homogeneous equilibrium $\text{A} + \text{B} \rightleftharpoons \text{C}$, is a question beyond the province of the Phase Rule. The composition axis is in terms of A and B, regardless of whether a phase is structurally $\text{AB} + \text{AB}_2$ or AB_2 minus some B, and of whether it consists entirely of the compound $\text{A} \cdot \text{B}$ or also partly of A and B in the proportions 1:1.

The ultimate indistinctness of the Phase Rule characterization of a "compound" is summarized in the following statement by Tammann:¹⁴ "On the basis of phenomena that fall in the field of pure thermodynamics a characteristic for chemical compounds can naturally not be deduced. For this, facts must be drawn upon which allow of an atomistic explanation." In practice, this atomistic or *chemical* point of view, then, must always form part of the background for the consideration or interpretation of phase diagrams.

In our discussion, then, decomposition, unqualified, means a heterogeneous reaction in which a compound produces two or more other phases of

¹² H. J. Emeleus and J. S. Anderson, *Modern Aspects of Inorganic Chemistry*, D. Van Nostrand, N. Y., 1938; A. E. Wells, *Structural Inorganic Chemistry*, Oxford University Press, London, 1945.

¹³ G. Hägg, *Nature*, **131**, 167 (1933).

¹⁴ (Ref. S-1), *Text Book of Metallography*, p. 374.

different composition; it must be distinguished from homogeneous decomposition, which may or may not be occurring in any phase, including that of the "pure" compound itself. Decomposition then will mean incongruent transition, but a congruent transition does not imply the presence of only a single species.

We now turn to the effect of the existence of solid binary compounds on the phase diagram.

B. Phase Diagram; General

If the congruent melting curve ($S = L$) and the congruent vaporization curve ($S = V$) of a compound meet, as do the fusion and sublimation curves of a single component, resulting in a triple point, we shall not treat it as a binary compound. The only possible binary effects would then arise in the liquid-vapor equilibria above the triple point, depending on the stability of the compound in the liquid and vapor states. In a binary compound, then, one or both of the transitions $S \rightleftharpoons L$ and $S \rightleftharpoons V$ will become incongruent before any equilibrium involving the compound C with both L and V can occur. But before studying the termini or intersections of these transition equilibria, whether congruent or incongruent, we shall first explain, with a few typical P/c and T/c sections, the meaning of congruent and incongruent transitions in phase diagrams.

At a pressure at which a compound melts congruently, the melting point of the compound is a maximum on the melting point curve, the composition of the liquid at the maximum being that of the solid compound. With all solids assumed to be pure, for simplicity of illustration, Fig. 7-3 then shows such an isobaric T/c diagram at a pressure above the triple points of the components. We are also assuming *positive slopes for all fusion curves*, whether of A , B , or C .

The melting point curve is continuous through the maximum T_c , and except for the flattening of this curve, compared to the limiting slopes of the freezing point curves of the components at T_A and T_B , the lower part of this diagram may be considered as two simple eutectic-type isobars set side by side. E_1 is the equilibrium Ae_1C and E_2 is Ce_2B . If B is added to solid A at the temperature T_x , A begins to dissolve, forming the liquid a on the curve T_Ae , and the relative amount of a increases until A is completely dissolved. The solution then remains unsaturated, as B is added, until the composition b is reached, when, at equilibrium, the compound C begins to precipitate. The composition of the solution b remains constant, but when the total composition c is reached, all the liquid has been consumed, leaving the solid C as the only phase. Further addition of B causes C to dissolve, forming

the solution d . If a solution of the composition c is cooled, it freezes (isobarically) at constant T , to the solid C , at T_c . If it is supercooled, it may behave according to the metastable extensions of the freezing point curves of the components, with a metastable eutectic at E' . The melting point of the compound T_c may be not only intermediate, as shown, but also higher than T_A or lower than T_B . The L/V loop is shown with a maximum, which may be on the right or left of the composition c ; the maximum may also be absent, leaving an "ascendant" L/V loop.

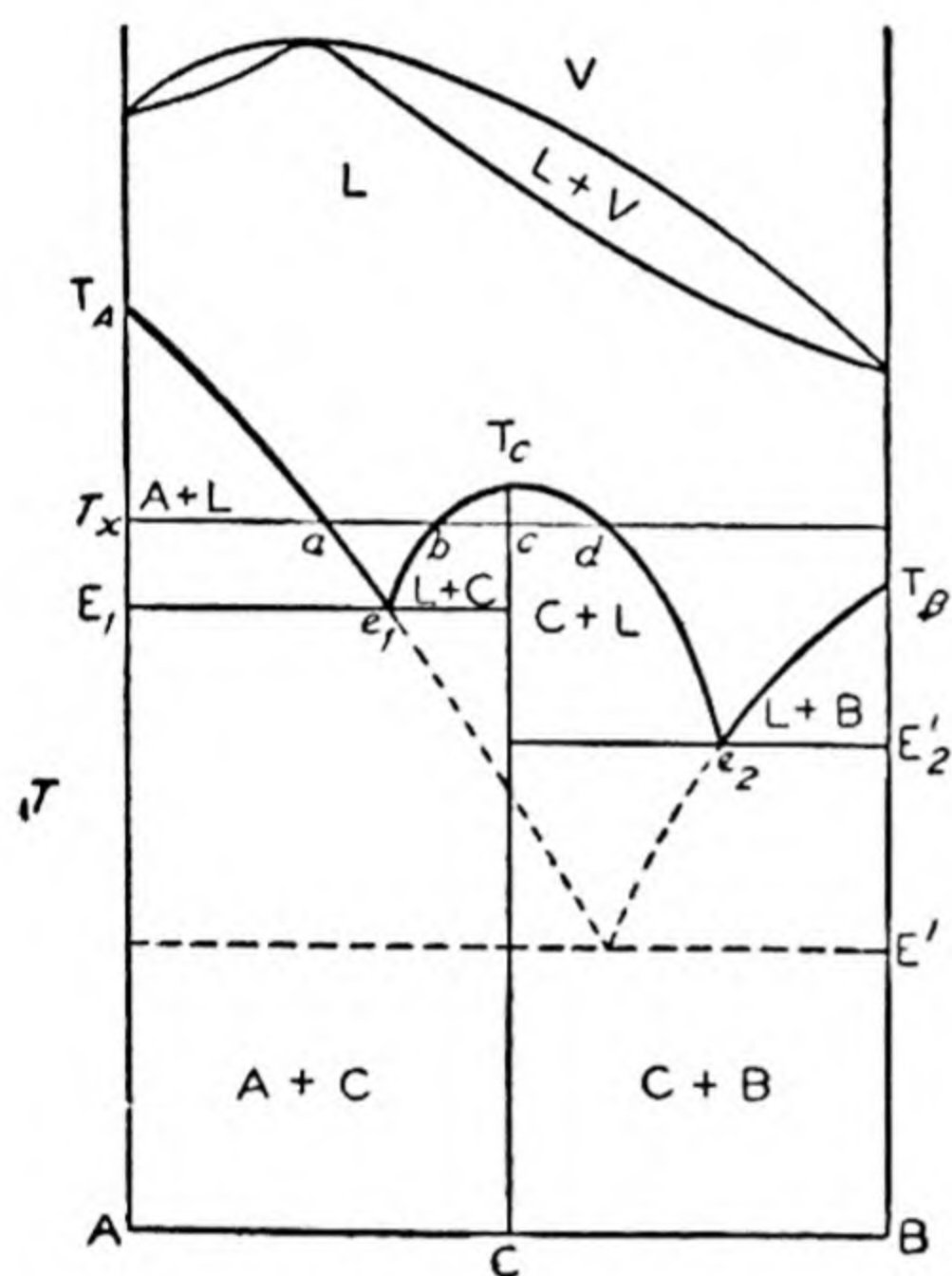


FIG. 7-3. $(T/c)_P$ diagram for congruently melting compound.

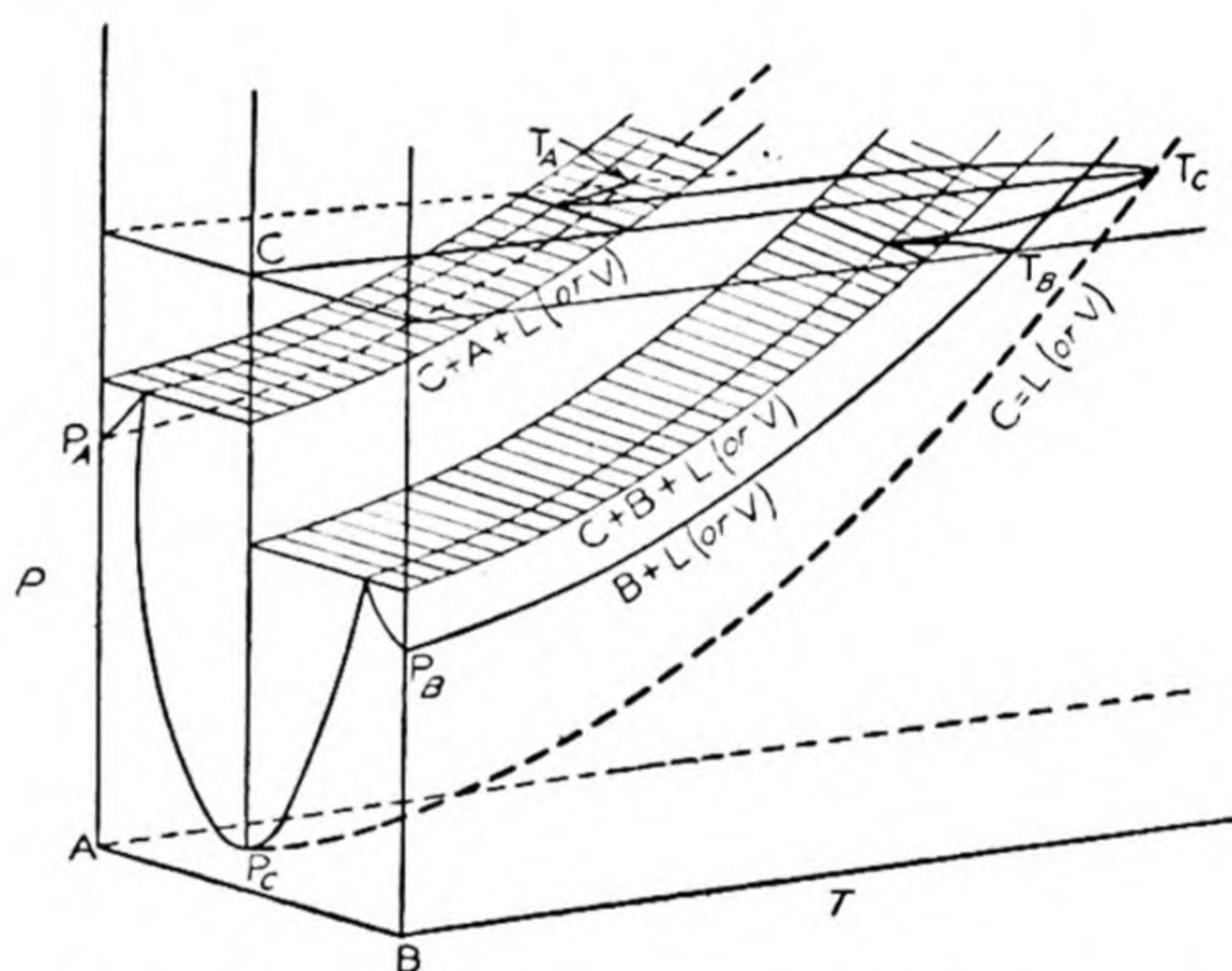


FIG. 7-4. $P/T/c$ relations for congruent transition of compound.

The same diagram, turned upside down, gives, in form, the P/c relations at constant T , at T above the triple points of the components; then the compound will be marked by a minimum (P_c) in the solid-liquid relations, the congruent melting pressure of the compound at the specified T . The schematic relation between the isobar and the isotherm may be seen in Fig. 7-4, showing the pertinent part of the space model of the system; T_A has here been made lower than T_B for clarity.

Fig. 7-3, moreover, with V for L and without the L/V loop, represents the congruent solid-vapor relations of a compound, at T and P below the triple points. Above the triple points, the components may be solid or liquid, depending on P and T , and the relations for congruent vaporization of C are as in Fig. 7-5. A variation of Fig. 7-5, in which both portions of the L/V loop have the same slope, will appear in some later diagrams (Figs. 7-48, 7-49). Again this diagram may be turned upside down (revolved about the line AB) to show the corresponding isobaric T/c relations, with a congruent sublimation temperature, T_c , of the compound.

As the stability of C relative to the system $A + L$ (or $A + V$) decreases, as by the effect of change in P and T , its melting (or sublimation) point (T_c , Fig. 7-3) may be said to fall relative to the equilibrium curves $T_A E' T_B$, and a point may be reached where T_c becomes submerged, or metastable, with respect to the $T_A E'$ curve. Beyond this P (or T) the transition of the compound is no longer congruent but incongruent. The singular point (type m) at which this change occurs is represented in Fig. 7-6. Beyond it,

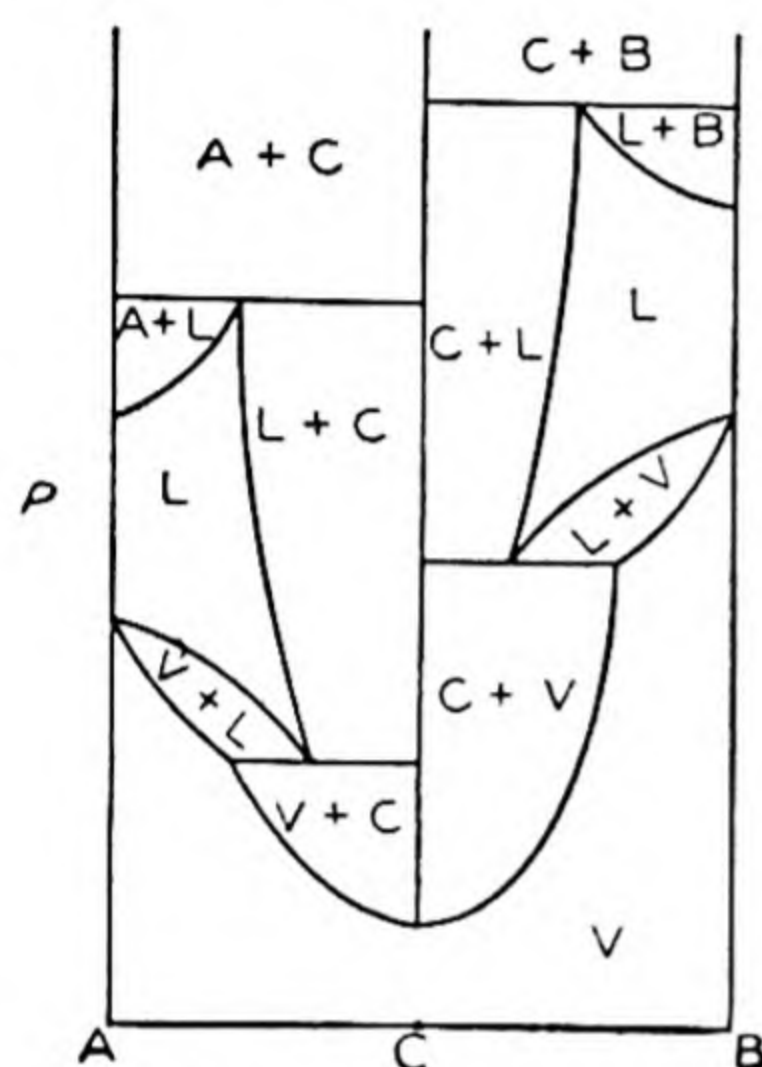


FIG. 7-5. $(P/c)_T$ diagram for congruently subliming compound.

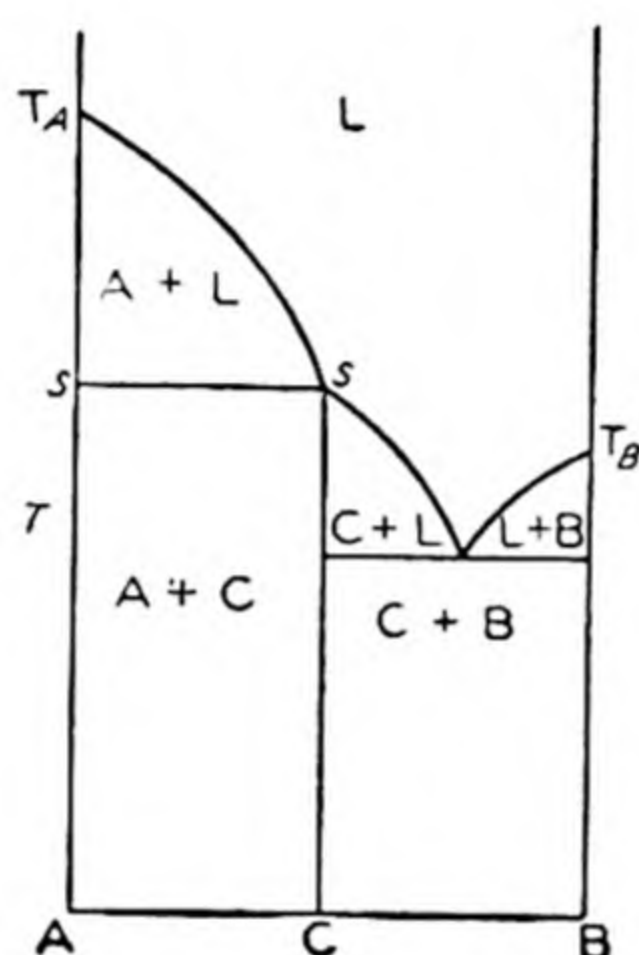


FIG. 7-6. $(T/c)_P$ diagram for singular point between congruence and incongruence of transition.

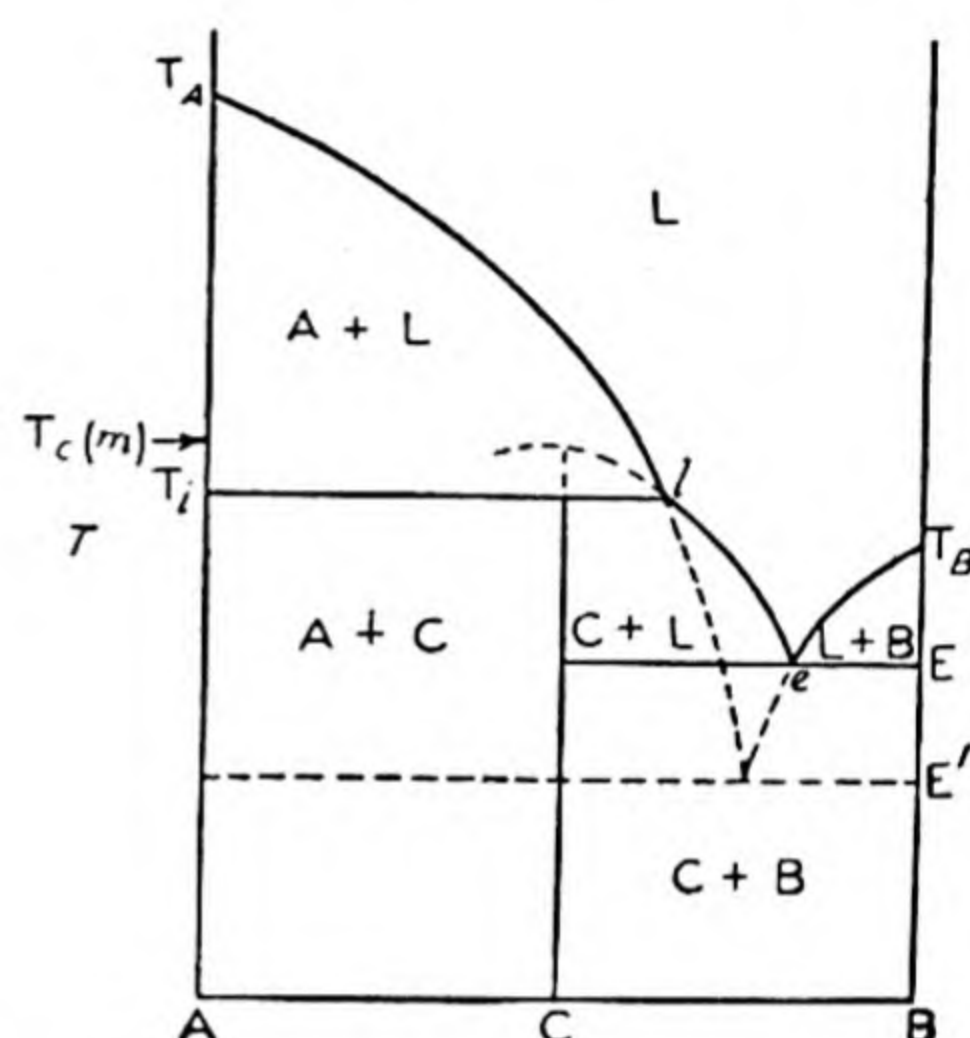


FIG. 7-7. $(T/c)_P$ diagram for incongruently melting compound.

in respect to P or T , the typical diagram of incongruent transition is that of Fig. 7-7.

Here E is the isobaric eutectic for the phases C , L , and B . T_i is the isobaric "transition point" of the compound, its incongruent melting point at the P of the section, or its decomposition temperature into A and L , the tie-line ACl ; $T_c(m)$ is its metastable congruent melting point. If a liquid with composition on the left of l is cooled, it first precipitates A and reaches isobaric invariance at T_i , whereupon the compound is formed by the reaction $A + l \rightarrow C + \text{cals.}$ If the total composition lies between A and C , the temperature begins to fall again only when the liquid l is all consumed, leaving $A + C$; if the composition is between C and l , A is all consumed, leaving the equilibrium $C + L$, and later, at E , there will be a second isobarically invariant halt for the eutectic, finally leaving $C + B$. If the composition is exactly C , only C is left. Again E' is the metastable eutectic of the system, involving A and B , if the compound fails to crystallize on cooling the liquid. T_i may be higher or lower than T_B .

Again these diagrams, 7-6 and 7-7, may be turned upside down to give

ing, and $C \rightleftharpoons A + V$ (T_i or P_i of Fig. 7-7 with V in place of L) for incongruent vaporization. A third type, $C \rightleftharpoons L + V$, arises, as we shall see later, only if the congruent melting point curve ($C = L$) reaches an equilibrium involving the vapor.

The plane of the compound may also be cut off by the univariant curves of the reactions $C \rightleftharpoons A + B$ and $C \rightleftharpoons L_1 + L_2$; the last, involving two liquid phases, will be discussed in Chapter VIII.

In the following discussion it will be assumed that the incongruence of the phase transition of the compound is always in respect to the component A , the incongruent melting being $C \rightleftharpoons A + L$, and the incongruent vaporization $C \rightleftharpoons A + V$.

C. Incongruent Transitions

1. The Equilibrium ACVB

In Fig. 7-9 the compound C is assumed to be formed from $A + V$ at low T , and to be cut off, as T rises, by the decomposition $C \rightleftharpoons A + B$, before any equilibrium involving liquid is reached. The binary lines in P/T

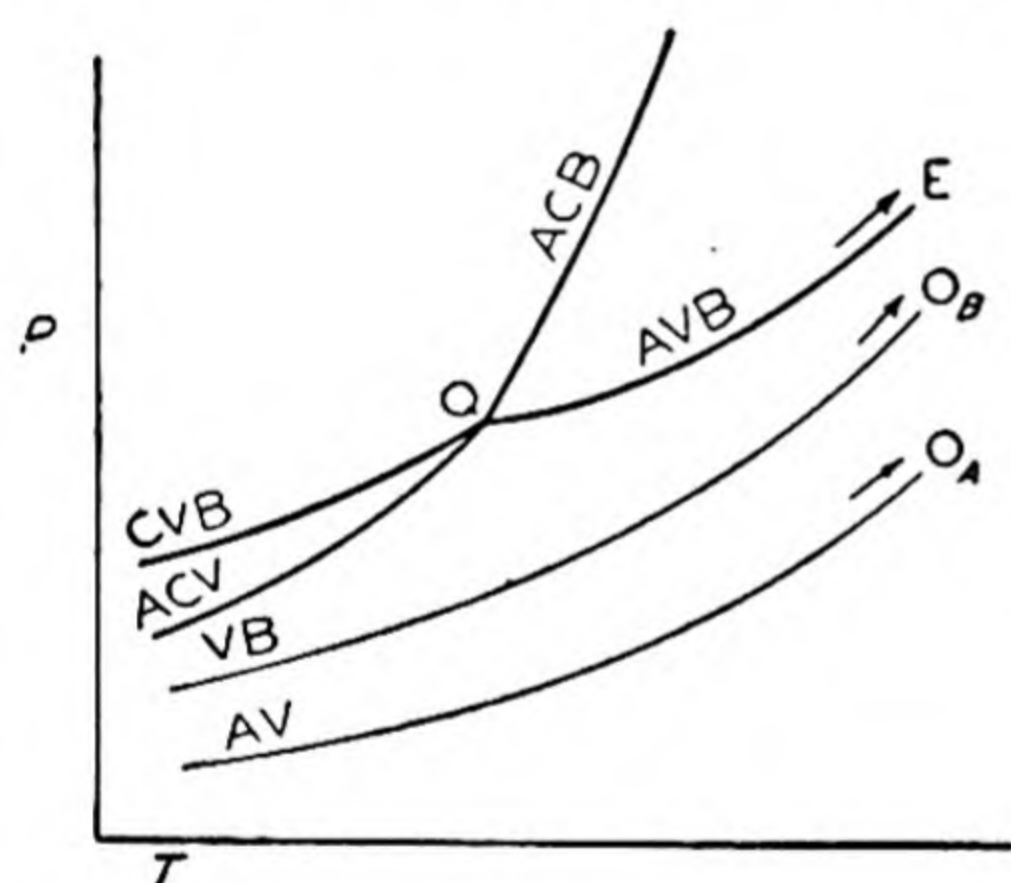


FIG. 7-9. The invariant point ACVB.

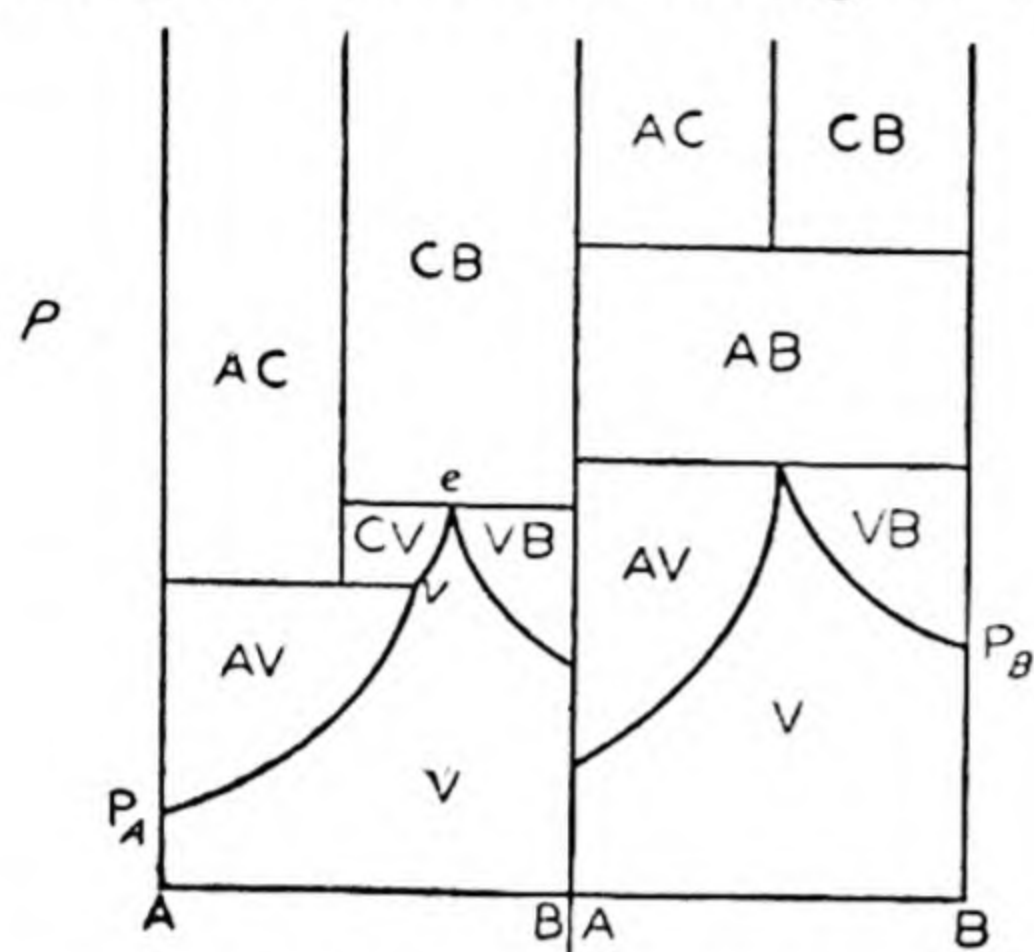
projection are 3-phase equilibria involving the phases marked, and they intersect at the quadruple "transition" point Q , for the phases $ACVB$. The C plane is limited by the $C \rightleftharpoons A + B$ decomposition curve on the right and by the $C \rightleftharpoons A + V$ curve at the bottom. The curve marked CVB is not a decomposition curve but the P/T curve for the vapor common to both C and B , the vapor being of intermediate composition. In section, see Fig. 7-10 for the isotherms and Fig. 7-11 for the isobars.

In this case, then, an equilibrium between C and L is possible only at high P (that is, above the vapor pressure of the system). Such an equilibrium would arise if the ACB decomposition curve, rising from Q , meets the eutectic curve ALB rising from the simple binary eutectic E , at a high pressure quadruple point Q_h involving $ACLB$, Fig. 7-12. Except for the phases involved, this quadruple point is similar to Q itself; the isobars at $P < Q_h$ and $P > Q_h$, for example, would be schematically identical with those of Figs. 7-11 (a) and (b) respectively, with L in place of V .

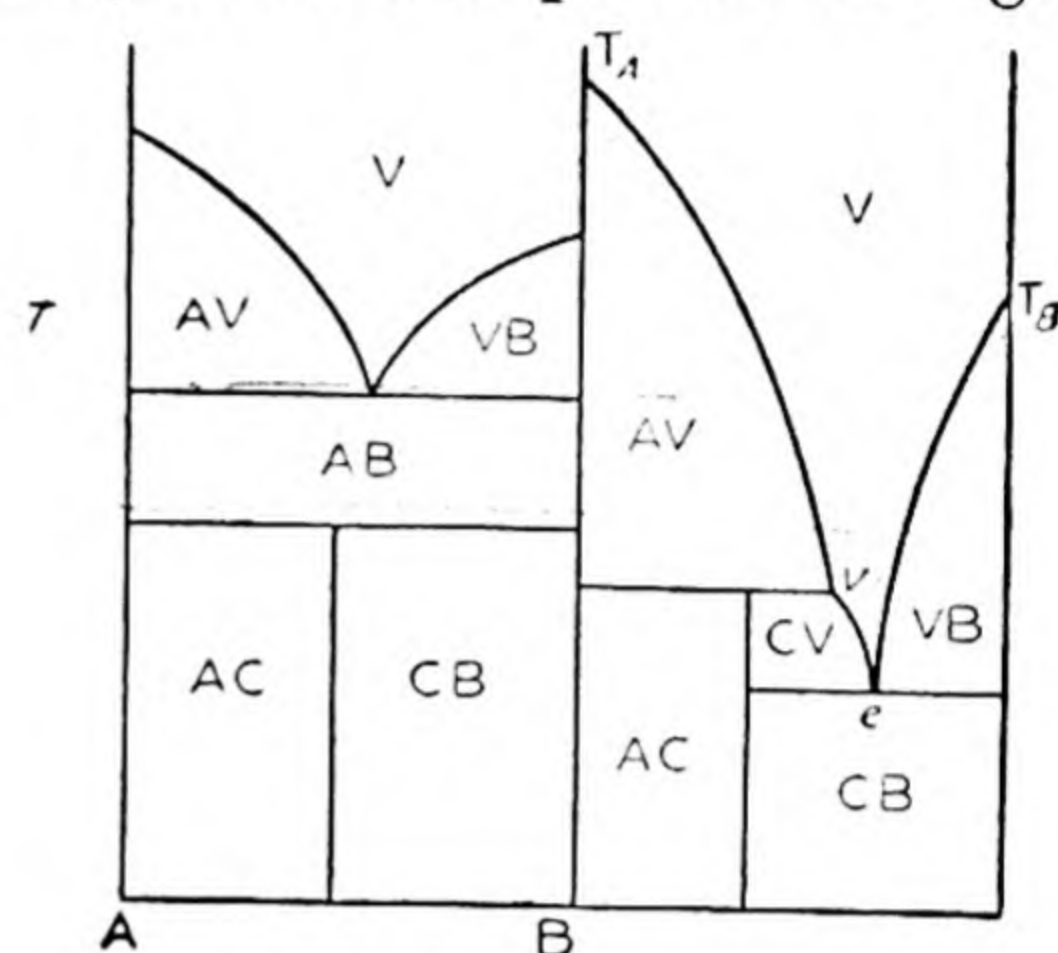
An invariant similar to Q would also mark the disappearance of the compound with decreasing T (Fig. 7-13), and it is then evidently possible that the existence of such a compound in a vaporization equilibrium may be

restricted to a limited range of T , between two such transition points, Q of Fig. 7-13 and Q of Fig. 7-9.

The crossing of the vaporus curves T_{Av} and ve at point v of Fig. 7-11(b) is analogous to the crossing of the solubility curves at point l in Fig. 7-7.



(a) $T < Q$



(b) $T > Q$

FIG. 7-10. Isotherms of Fig. 7-9.

FIG. 7-11. Isobars of Fig. 7-9.

A similar significance is seen in the crossing of the vaporus curves at point v in the isotherm of Fig. 7-10 (a). If x_B is the mole fraction of B in the vapor, it is clear that the slope dP/dx_B for the vaporus of the equilibrium $A + V$ must be greater than dP'/dx_B , that of the vaporus of the equilibrium $C + V$, at their intersection at point v , where the pressure is P_v . If the vapor is assumed to be ideal and made up entirely of the separate

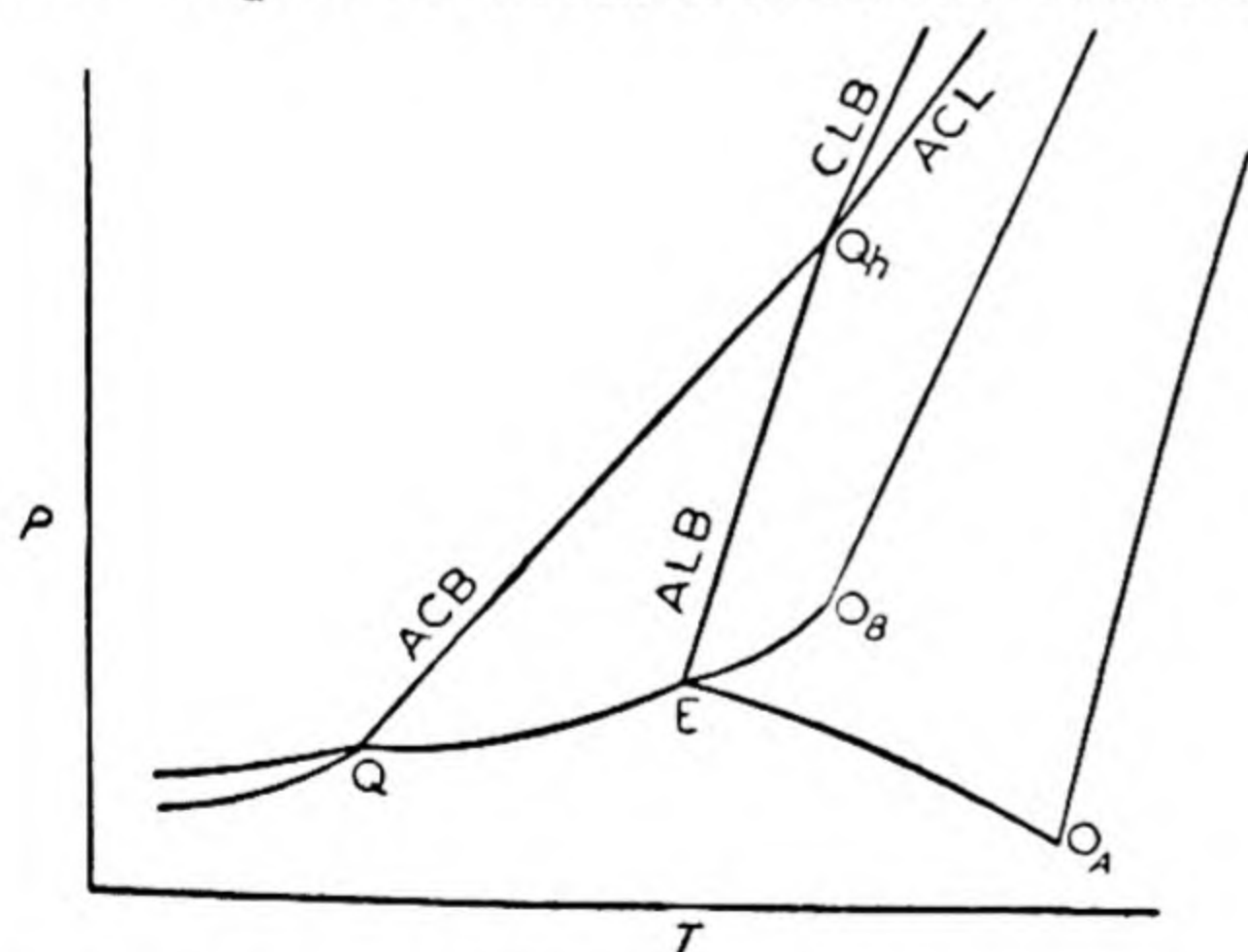


FIG. 7-12. The high pressure invariant point ACLB.

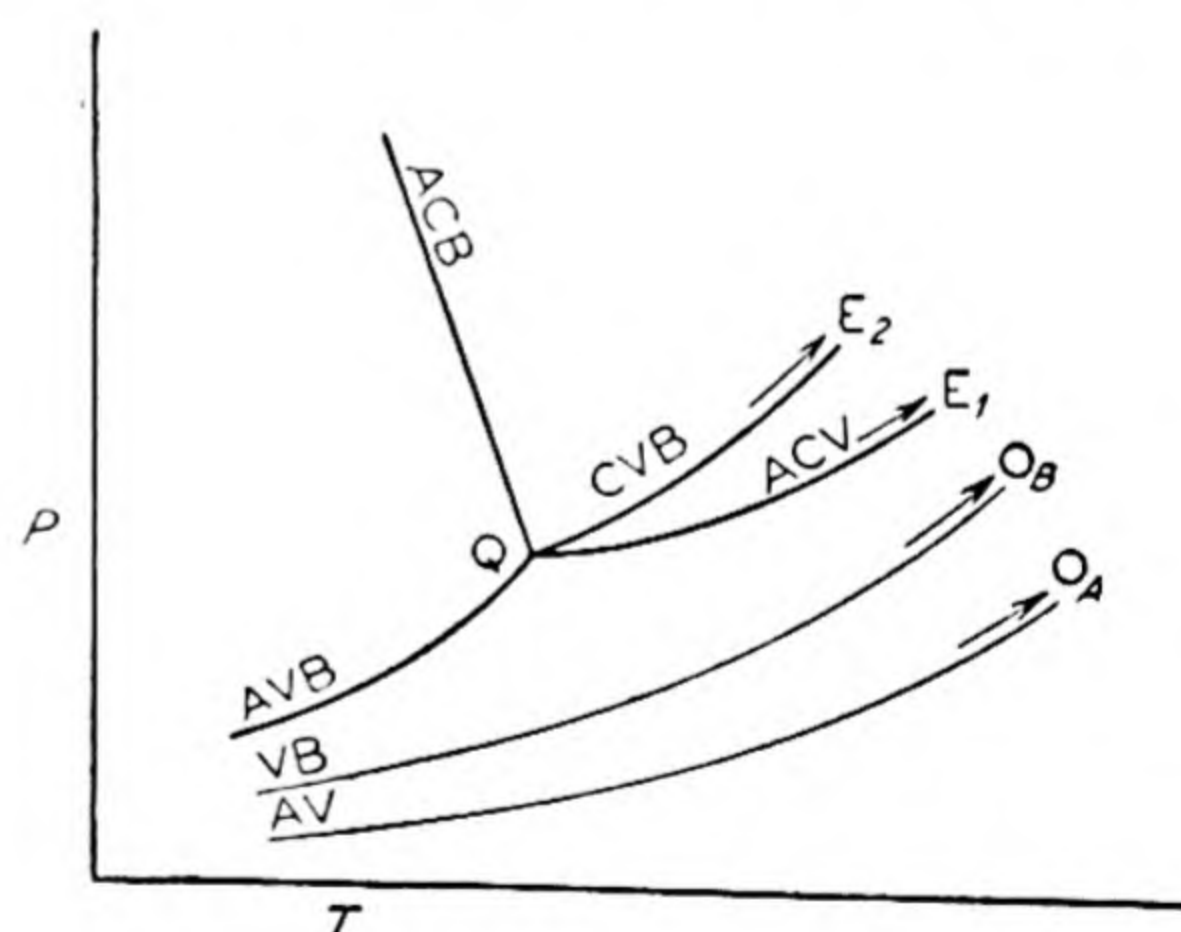


FIG. 7-13. The invariant point ACVB (variation of Fig. 7-9).

species A and B, the ratio of the slopes at point v may be related to the composition of the compound C. For equilibrium between vapor and solid A the condition is $x_A P_v = P_A$, in which P_A is the vapor pressure of pure A; hence the slope of the $A + V$ vaporus at v is

$$\frac{dP}{dx_B} = \frac{P_v^2}{P_A}. \quad (1)$$

For equilibrium with solid C at point v the additional condition is a constant value of $(x_A P_v)(x_B P_v)$ if the composition of the compound C is A·B; the slope of the vaporus of C + V at the same point v is therefore

$$\frac{dP'}{dx_B} = \frac{P_v^2}{2P_A} \left(\frac{P_v - 2P_A}{P_v - P_A} \right). \quad (2)$$

Hence the ratio of the slopes is

$$\frac{dP'}{dP} = \frac{1}{2} \left(\frac{P_v - 2P_A}{P_v - P_A} \right), \quad (3)$$

which reduces to $\sim \frac{1}{2}$ if the vapor pressure of A is negligibly small. If C = A·2B,

$$\frac{dP'}{dx_B} = \frac{P_v^2}{3P_A} \left(\frac{P_v - 3P_A}{P_v - P_A} \right), \quad (4)$$

or the ratio of the slopes $\cong \frac{1}{3}$; while if C = 2A·B,

$$\frac{dP'}{dx_B} = \frac{P_v^2}{3P_A} \left(\frac{2P_v - 3P_A}{P_v - P_A} \right), \quad (5)$$

and the ratio $\cong \frac{2}{3}$ if P_A is small compared to P_v .

2. The Equilibrium ACLV; Compound with Incongruent Melting Point

The more interesting cases involve equilibria between C and both L and V together. Now we may assume a C plane cut off on the right by an incongruent melting or decomposition curve, ACL, and at the bottom by an incongruent vaporization or decomposition curve, ACV, the two meeting at a quadruple "transition" point, Q_1 , for the phases ACLV; the order will be L-V if the vapor is richer than L in respect to B, which will be the case if the L/V loop is assumed ascendant throughout (Fig. 7-14).

The point Q_1 is the intersection of two decomposition curves, ACV and ACL, and two solubility curves, ALV of solid A and CLV (C not the middle phase) of the compound. For cross-sections, Fig. 7-15 shows isotherms, and Fig. 7-16 shows isobars.

Both Q (Fig. 7-9) and Q_1 (Fig. 7-14) are 4-phase invariant points at the pressure of the system, and in either case the system, with all four phases present, maintains itself, at equilibrium, at constant T (and P) until one of the phases is gone. Only the second type Q_1 is of practical importance, however, as it involves the liquid phase, which helps to maintain equilibrium, especially if the concentration of A in it is high. It can be reached by heating (at the pressure of the system or in open air if the vapor pressures are less than 1 atm) mixtures of A and C or of C and its saturated solution, or by cooling the saturated solution of A, that is, along curves ACV or CLV

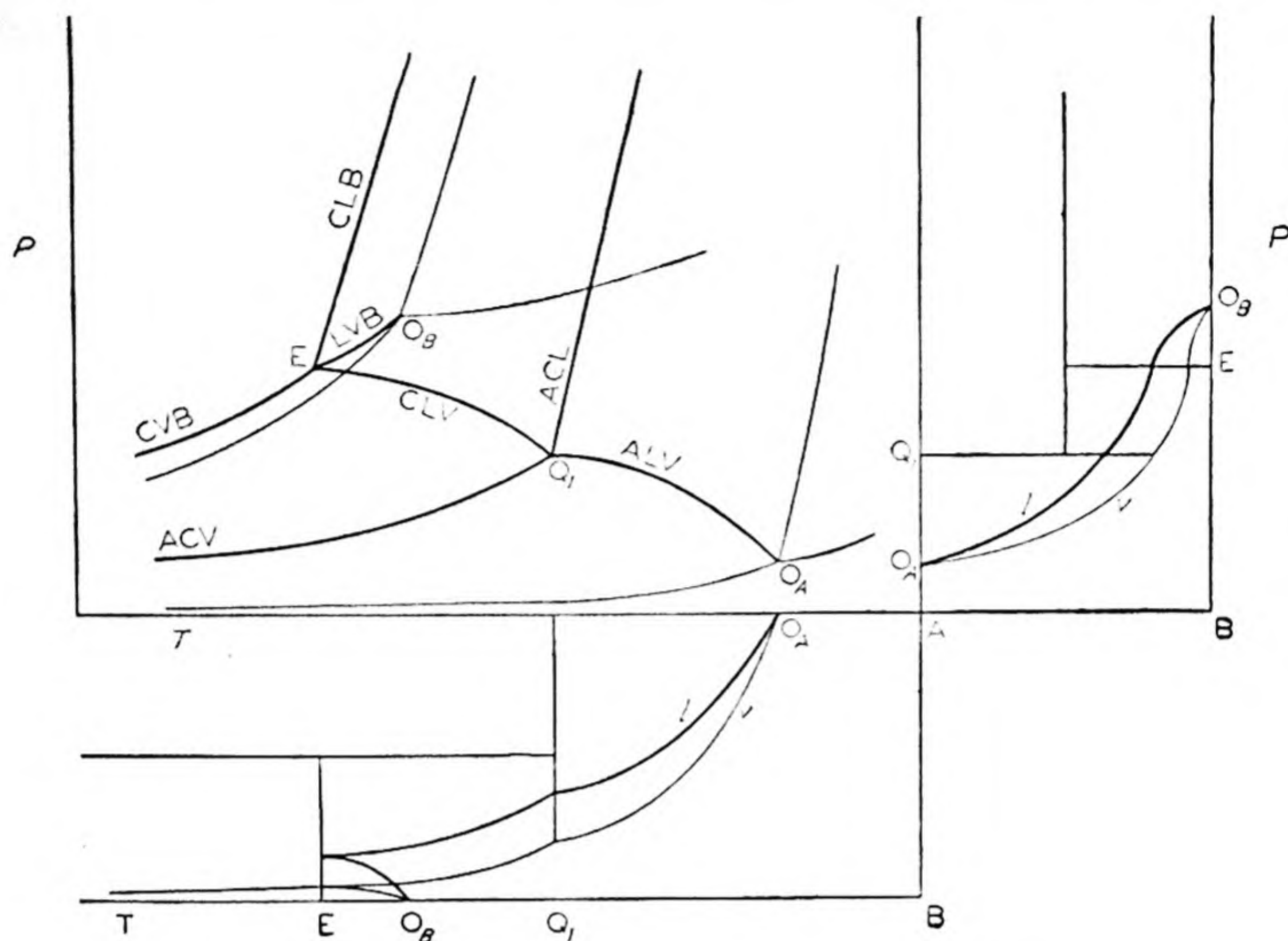


FIG. 7-14. The "transition point" ACLV.

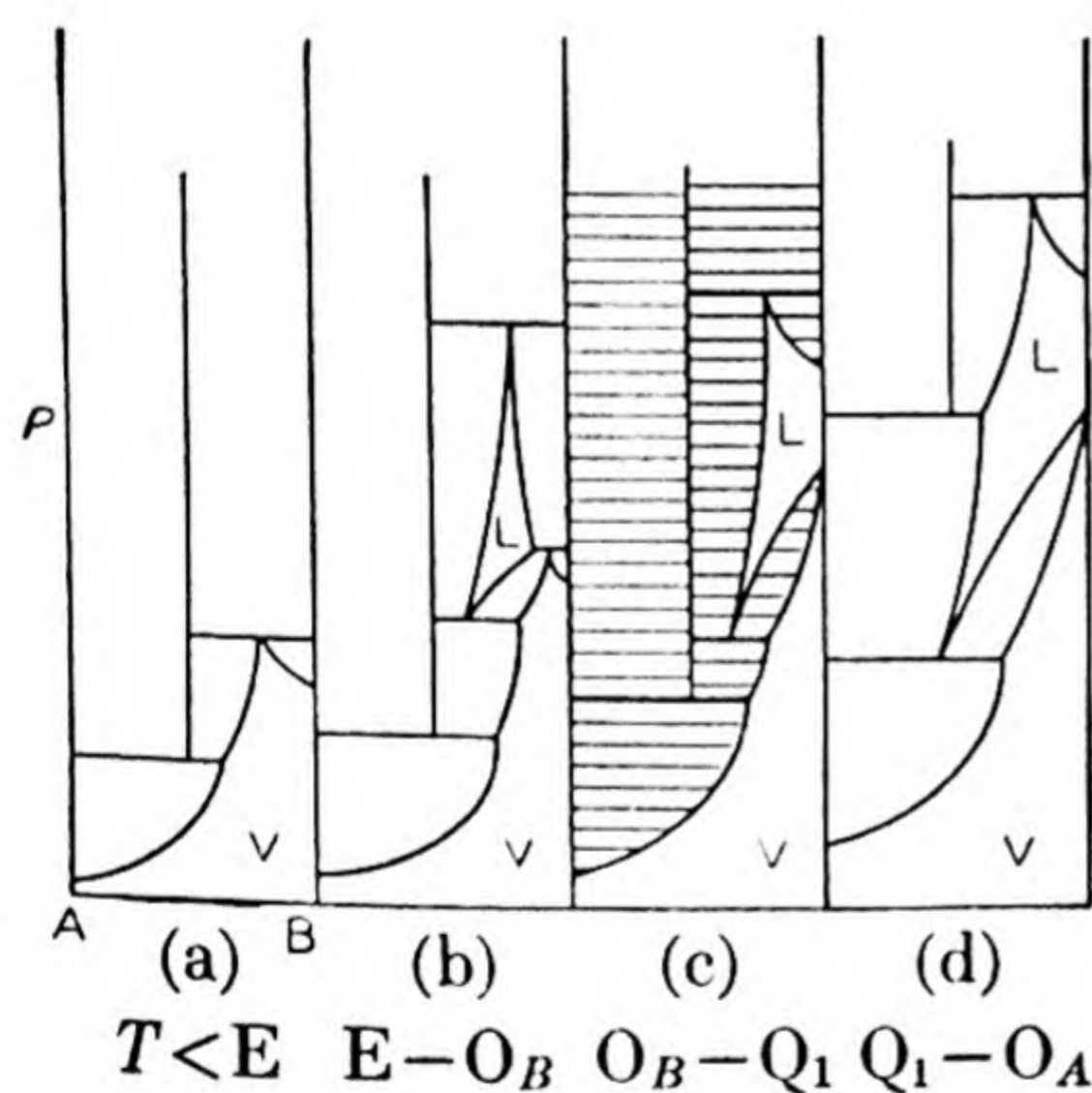


FIG. 7-15. Isotherms of Fig. 7-14.

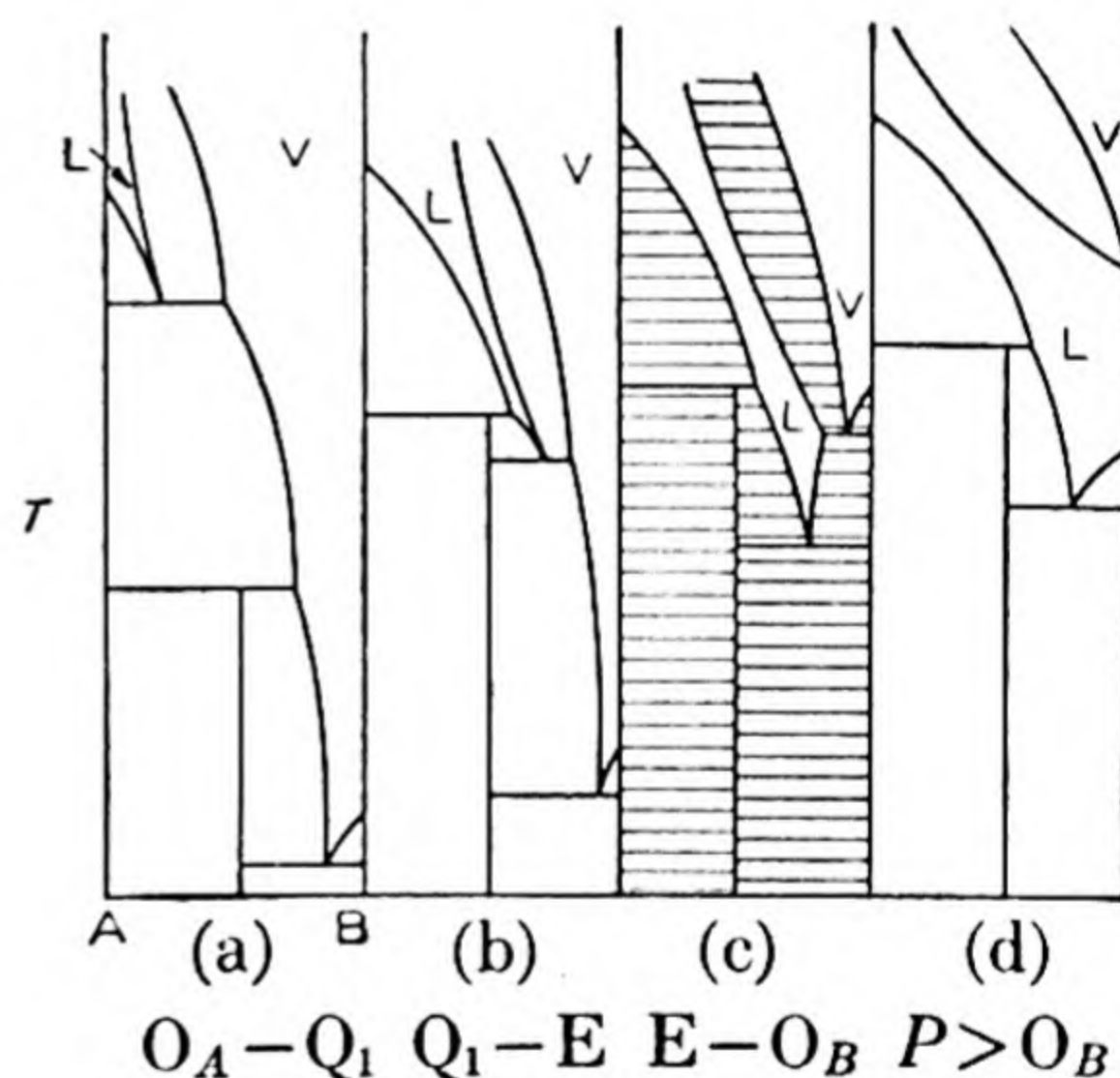


FIG. 7-16. Isobars of Fig. 7-14.

with rising T , or along curve ALV with falling T . A familiar example of this type of invariant is the "transition point" of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the temperature of the "normal" invariant (open air at 1 atm P) being 32.383° , with 33.20% Na_2SO_4 , by weight, in the solution.¹⁵ Because of the high heat of transition involved, the mixture $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Na_2SO_4 , and saturated

¹⁵ H. C. Dickinson and E. F. Mueller, *J. Am. Chem. Soc.*, **29**, 1381 (1907). The aqueous vapor pressure of the system at the quadruple point is 30.8 mm; E. Cohen, *Z. phys. Chem.*, **14**, 53 (1894).

solution is useful as a thermometric standard and as a heat reservoir of constant temperature.

The point Q_1 is the intersection of three univariant "vapor pressure curves," ACV, CLV, and ALV. The intersection of any two of these curves, like the intersection of the two *solubility* curves, CLV and ALV, fixes the temperature of Q_1 . With particular reference now to the curve ACV, we may note that if these are pure phases, such as, presumably, pure Na_2SO_4 (A), pure $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (C) and pure H_2O vapor (V), then the vapor pressure curve ACV, involving the equilibrium of exactly these three pure phases, will always be the same, whatever the nature of the possible liquid phase of the system. If the liquid, then, contains additional non-volatile solutes not forming solid solution with the solids A and C, the ACV curve, remaining binary, will not be affected, while both the CLV and the

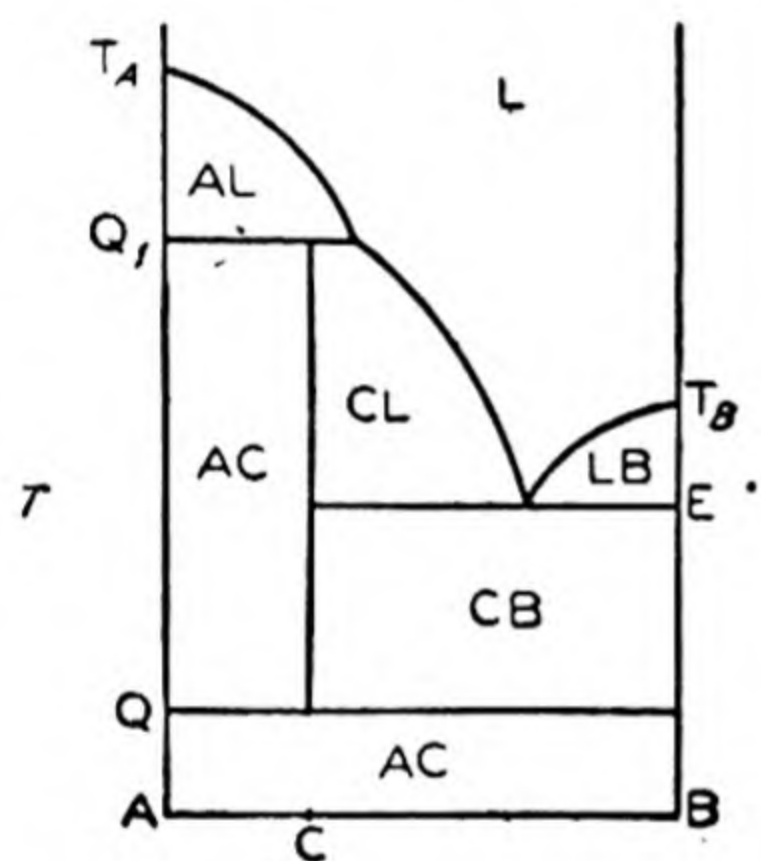


FIG. 7-17. Decomposition of compound below the eutectic.

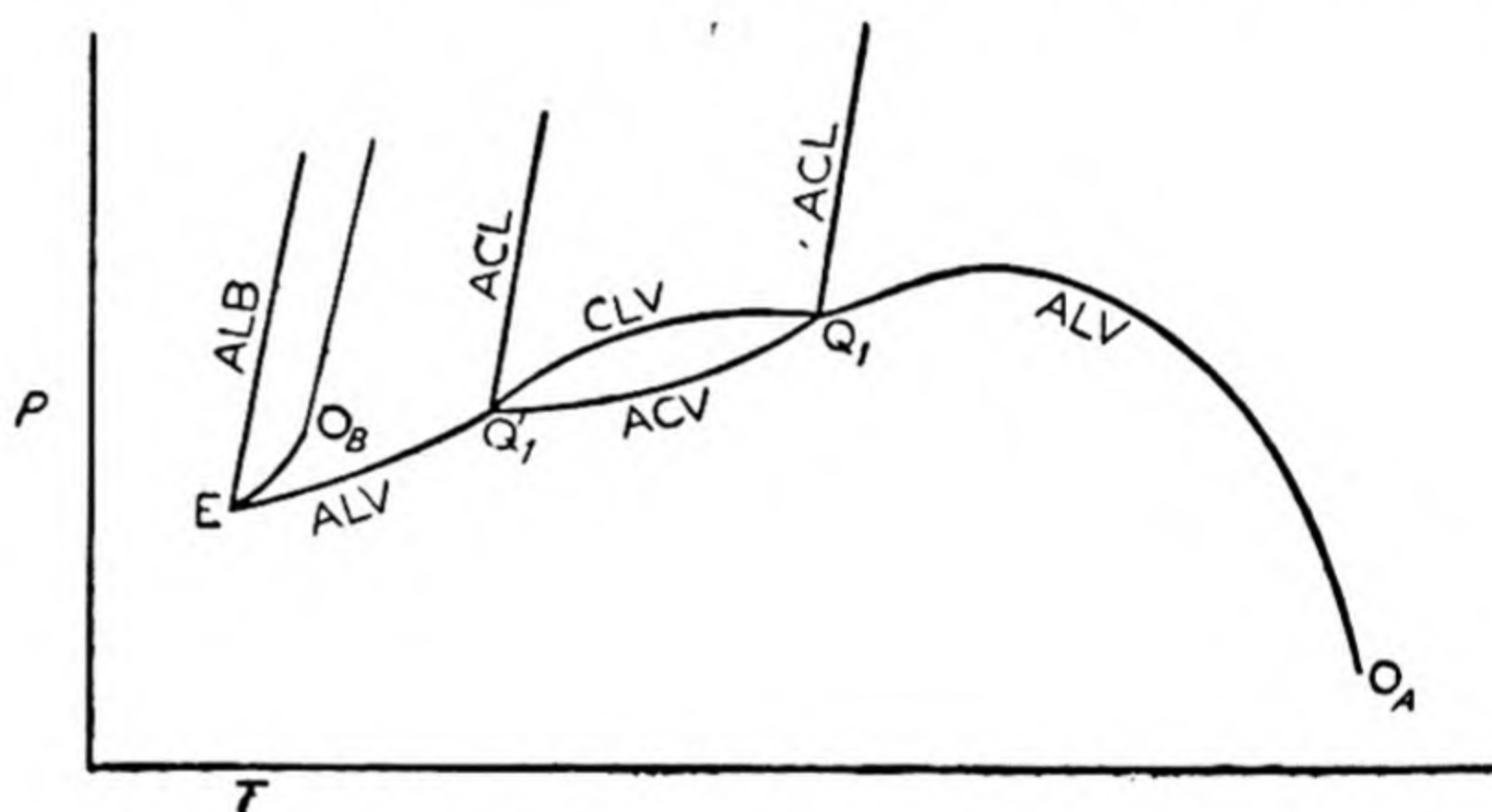


FIG. 7-18. Compound with "inverse fusion" point.

ALV curves will be lowered, the vapor pressures of the saturated solutions being lowered by the additional solutes, at any given temperature. The result is the lowering of the transition temperature Q_1 .

As for the course of the decomposition curves originating at Q_1 , the ACV equilibrium may end at some lower T at a transition point of the type of Q of Fig. 7-13; the condensed diagram then appears as in Fig. 7-17. As an example, the compound Fe_2Sn decomposes, on cooling, to $\alpha\text{-Fe} + \text{FeSn}$, at $\sim 760^\circ$.¹⁶ Another possibility is a second ACLV transition point Q_1' , reached if the ACV curve, in its course to lower T , intersects again the solubility curve CLV of the compound, thereby terminating it at a lower transition point above the eutectic of the system. This, of course, is possible only if the solubility curve CLV has a positive P/T slope at least for

¹⁶ C. A. Edwards and A. Preece, *Iron and Steel Inst.*, **124**, 41 (1931); see also Hansen, *loc. cit.*, p. 739; according to F. Wever and W. Reinecken, *Z. anorg. Chem.*, **151**, 349 (1926) it is the compound Fe_3Sn which decomposes on cooling, at $\sim 890^\circ$, to $\alpha\text{-Fe}$ and FeSn_2 .

part of its course, since the ACV curve, a decomposition reaction forming vapor, must have a positive slope throughout. Hence we may have Fig. 7-18, in which the C plane is bounded by the ACL curves (from Q_1' and Q_1) on its sides, and by the ACV curve at the bottom. The solubility curve of A is therefore here temporarily interrupted by that of the compound, as seen in the condensed diagram of Fig. 7-19. The point Q_1 of this system is

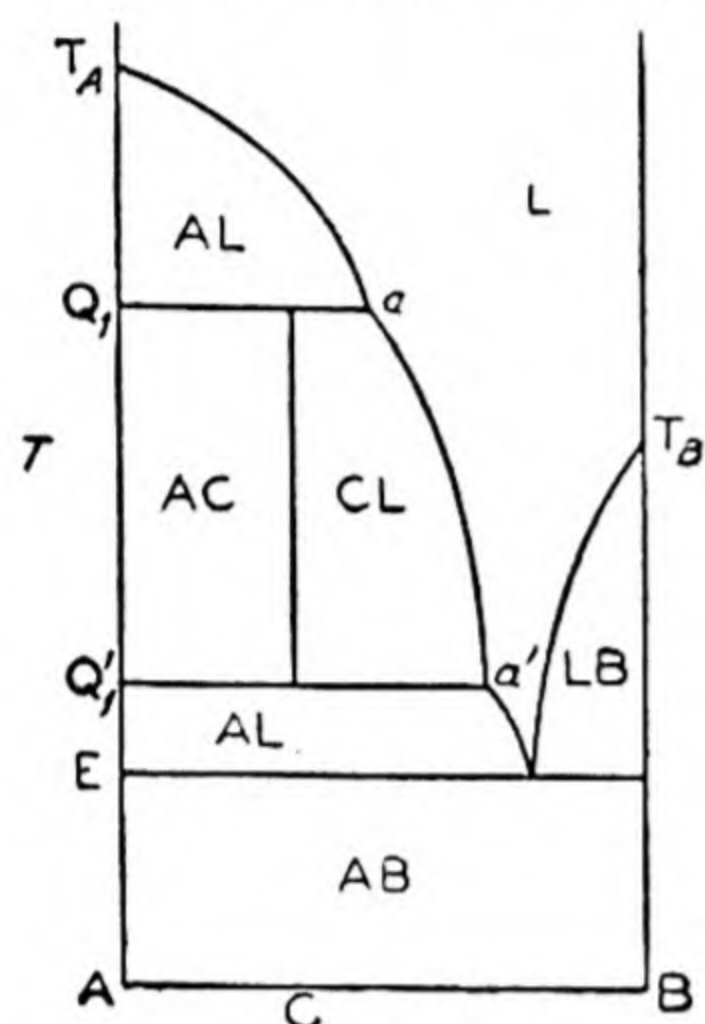


FIG. 7-19. Condensed diagram of system of Fig. 7-18.

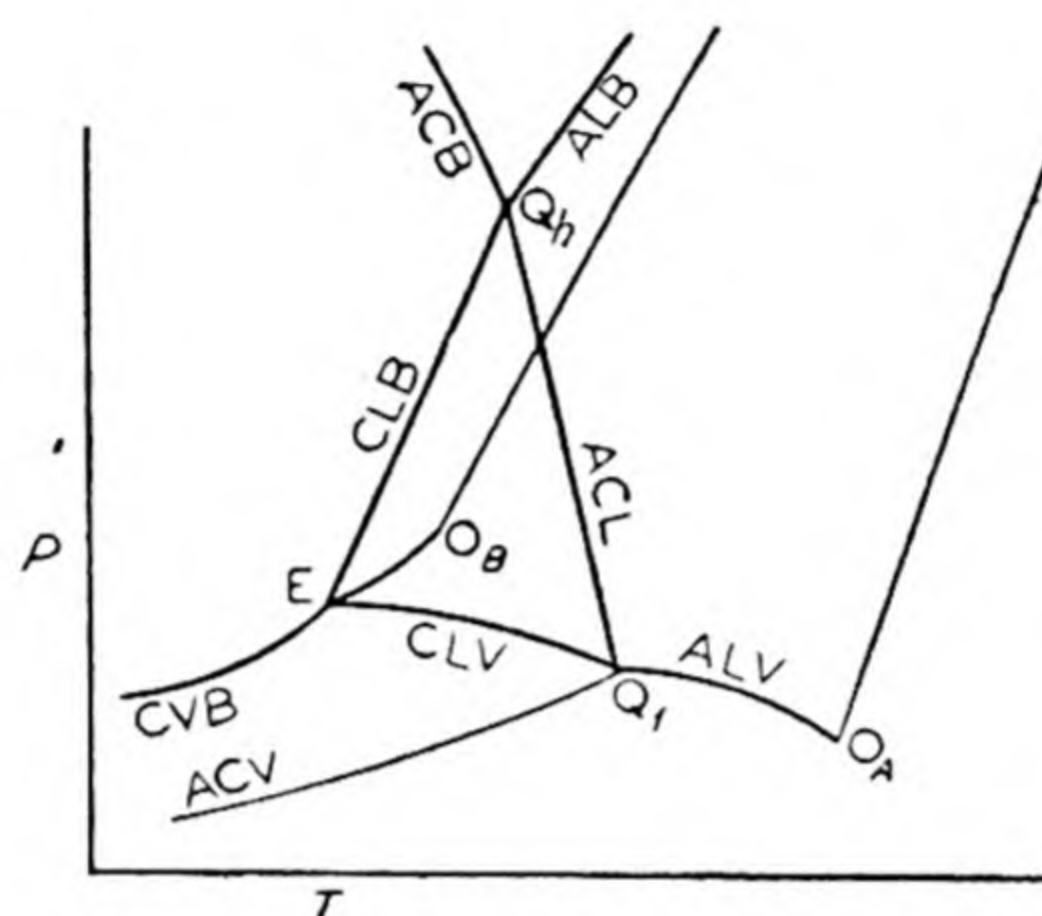


FIG. 7-20. Variation of Figs. 7-12 and 7-14.

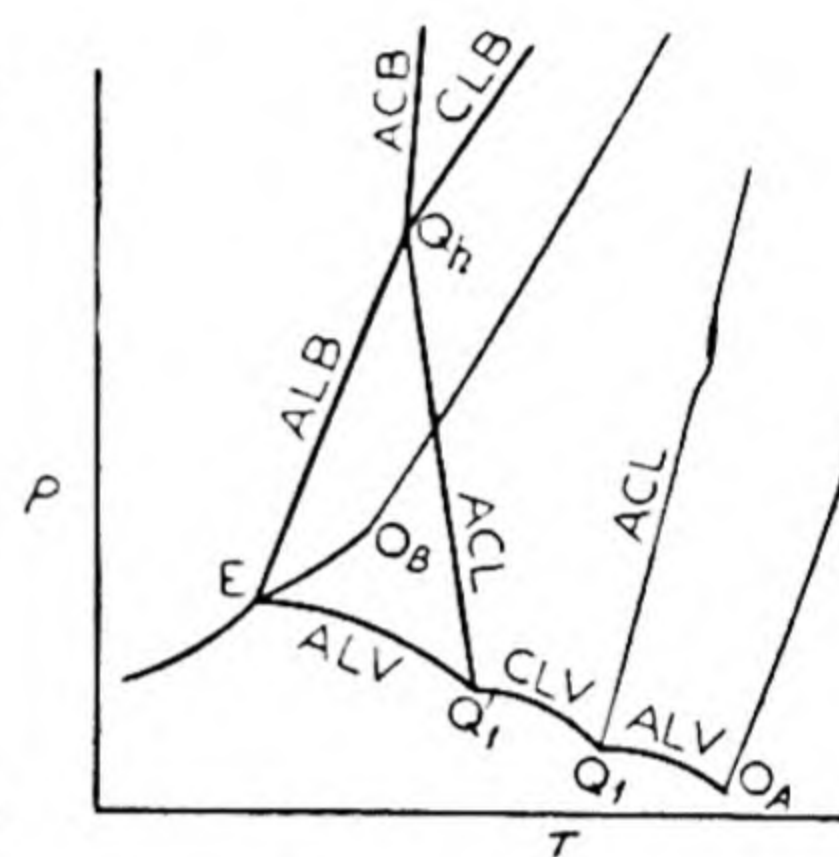


FIG. 7-21. Variation of Fig. 7-18.

called a peritectic point, because at this temperature the solid C melts on heating to a liquid a + a second solid (A). Similarly the solid C melts on cooling, at Q_1' , to a liquid a' + a second solid (A); hence this is sometimes referred to as "inverse fusion," and we may call Q_1' an inverse peritectic. As an example, $\text{Ce}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ melts, on cooling, to liquid + $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, at $\sim 33^\circ$.¹⁷

The ACL curve of Fig. 7-14 may terminate at an intersection with a decomposition curve ACB, at a high pressure invariant point, Q_h , on the eutectic curve CLB, as in Fig. 7-20. In this case Fig. 7-11, with L in place of V, again gives the schematic isobars, with Fig. 7-11(a) at $P > Q_h$ and 7-11(b) at $P < Q_h$. In Fig. 7-18 the two ACL curves may form a closed curve, with rising P , giving a completely limited field for the existence of the compound; on the other hand, the curve originating from Q_1' may reach a high pressure invariant (Q_h of Fig. 7-21) on the eutectic curve, meeting the decomposition curve ACB. In this case an isobar just below Q_h would be that of Fig. 7-19, and one just above Q_h that of Fig. 7-17.

Finally, either or both of the decomposition curves of Fig. 7-14 may change to curves of congruent transition, at singular points of the type shown in Fig. 7-6.

¹⁷ J. Koppel, *Z. anorg. Chem.*, **41**, 377 (1904); verified by N. H. J. M. Voogd, *Rec. trav. chim. Pays-Bas*, **52**, 768 (1933).

3. Many Compounds

Let us now suppose that three solid compounds are formed, numbered 1, 2, 3 with increasing proportion of the more volatile, lower melting component B, pure A being compound 0. In the region below the eutectic, the P/T relations would be schematically those of Fig. 7-22; the curve

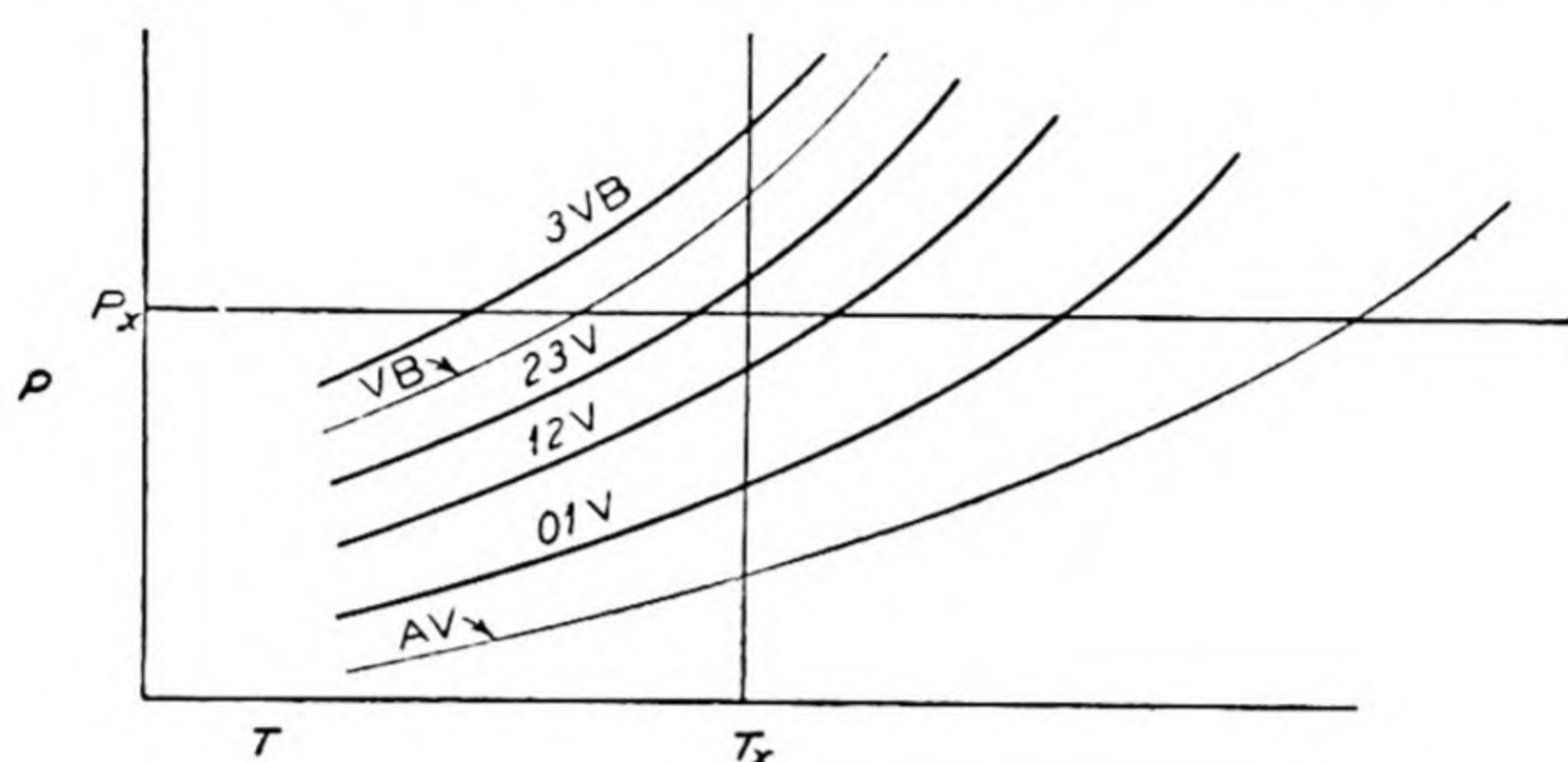


FIG. 7-22. Vapor pressure curves involving several compounds.

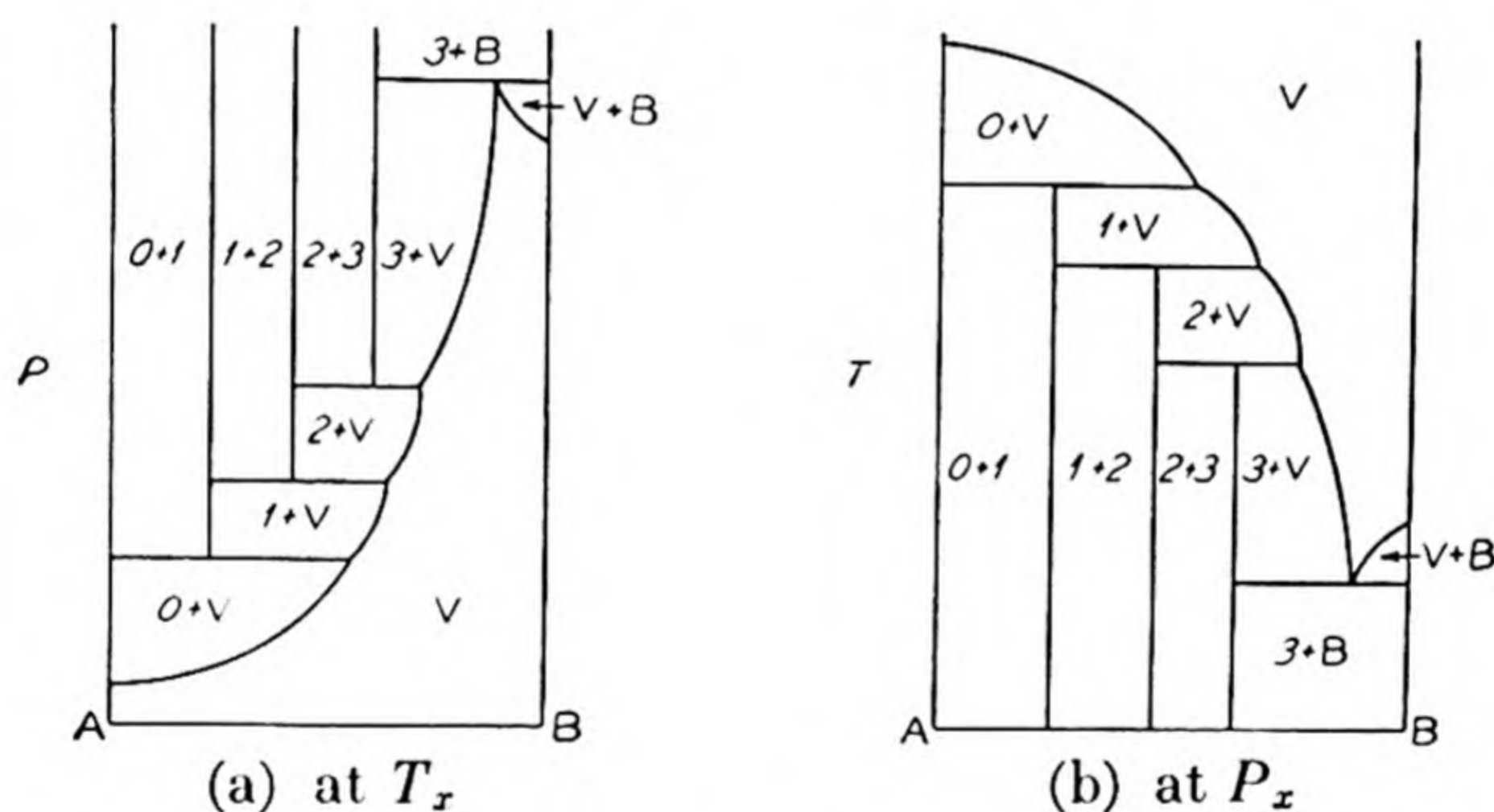


FIG. 7-23. Isotherm and isobar of Fig. 7-22.

01V is the decomposition curve for the first compound, the 3-phase univariant reaction $1 \rightleftharpoons 0 + V$; the curve 12V the decomposition curve for the second compound, or $2 \rightleftharpoons 1 + V$; and the next for the decomposition $3 \rightleftharpoons 2 + V$. Fig. 7-23(a) is the isotherm at T_x , giving therefore the equilibrium pressure for the formation of each compound from a lower compound (or for its decomposition to a lower compound), at the specified T . The isobar (Fig. 7-23(b)) gives, then, the equilibrium temperatures of decomposition of each hydrate, at the specified pressure P_x .

If the decomposition curve of compound 2, 1-2-V, meets the solid-solid decomposition curve $2 \rightleftharpoons 1 + 3$, the compound 2 ceases to exist stably in contact with vapor or "at the pressure of the system"; its disappearance

with rising T is shown, in projection, in Fig. 7-24(a), and with falling T , in Fig. 7-24(b). The invariant point Q' involves in either case the phases $123V$. The cross-sections for Fig. 7-24(a) are shown in Fig. 7-25; in this the vapor phase composition is omitted, as is usually done when A is so non-volatile that the vapor is practically pure B.

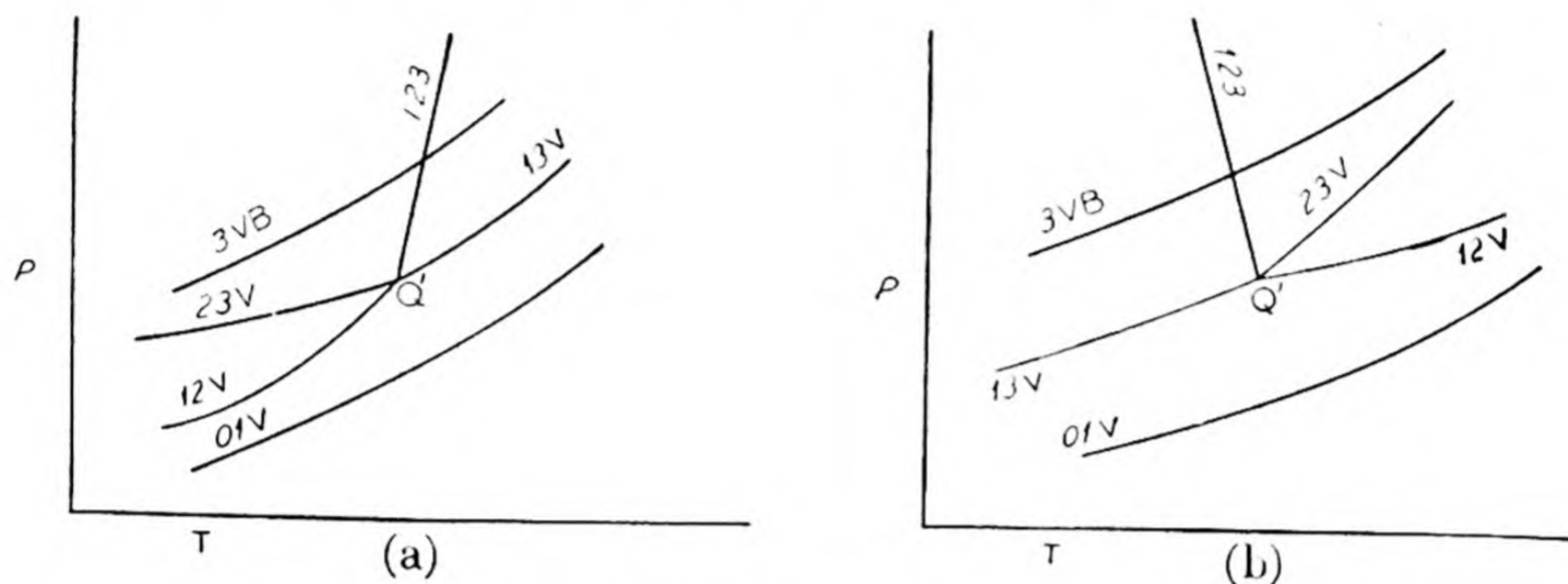


FIG. 7-24. The invariant point $123V$.

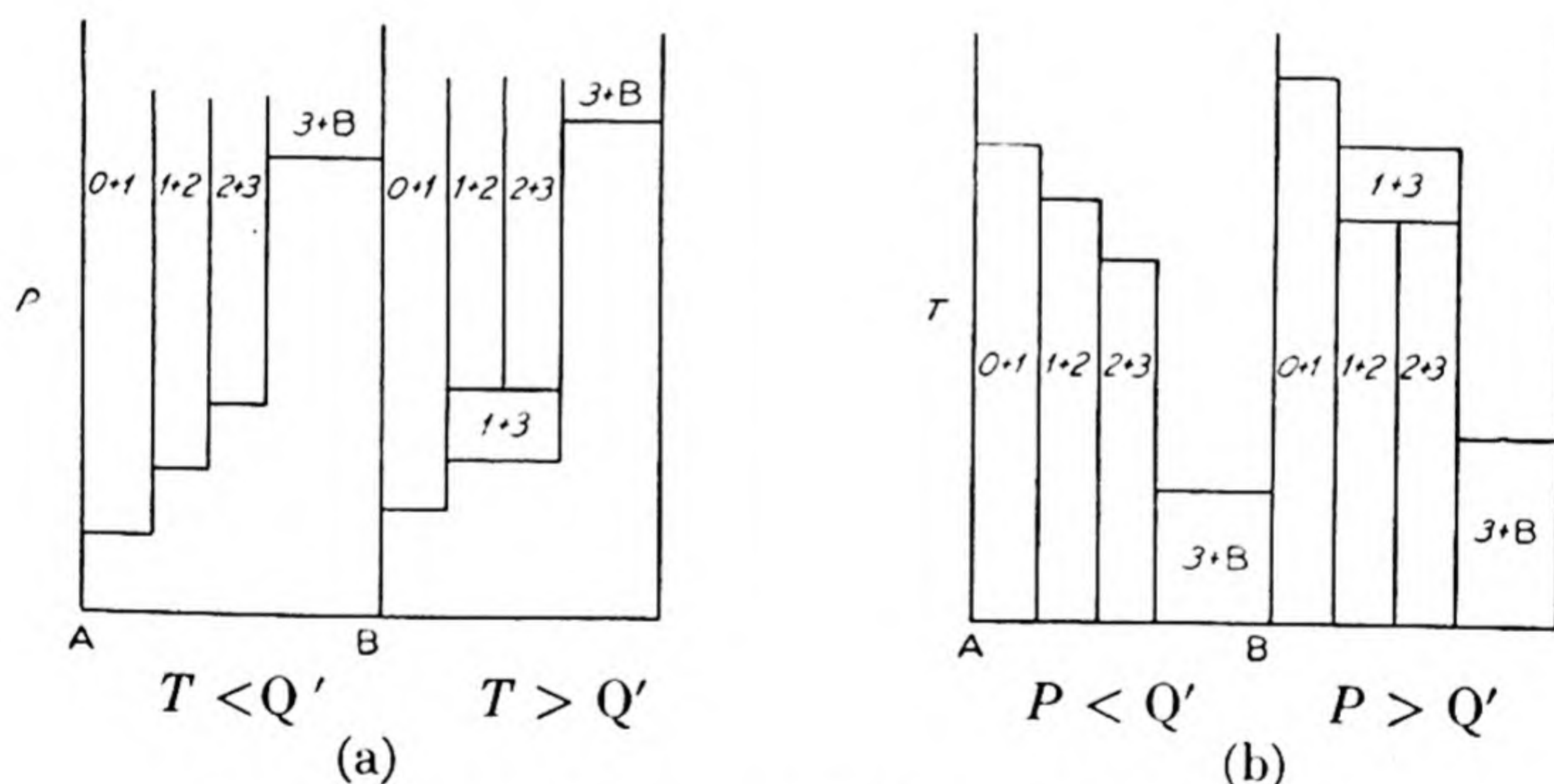


FIG. 7-25. Isotherms and isobars of Fig. 7-24 (a)

If all the three compounds of Fig. 7-22 reach equilibrium with liquid, so that each has a solubility curve, as for C of Fig. 7-14, the schematic relations are those of Fig. 7-26. The quadruple points, Q_1 , Q_2 , Q_3 , are all similar in nature and may be called the "transition points" of the compounds 1, 2, 3, respectively. The eutectic now involves the phases $3LVB$. The isotherm of Fig. 7-27(a), just below Q_2 , shows that below the transition point Q_2 the solubility s_1 of compound 1, now metastable in contact with L and V, is greater than that (s_2) of the stable solid compound 2; above Q_2 (Fig. 7-27(b)) the solubility of compound 2, now metastable, is greater than that of compound 1.

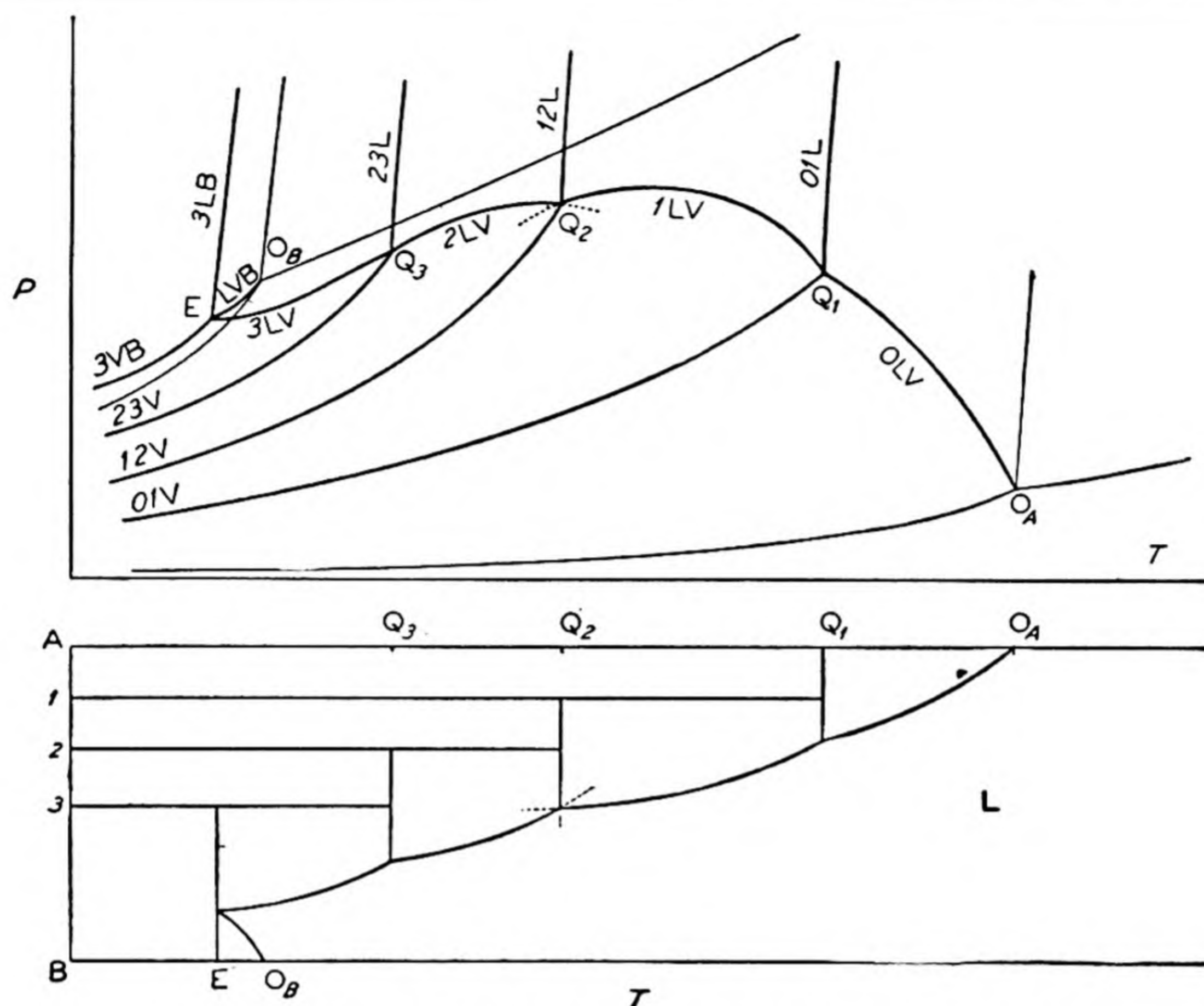


FIG. 7-26. Several incongruently melting compounds.

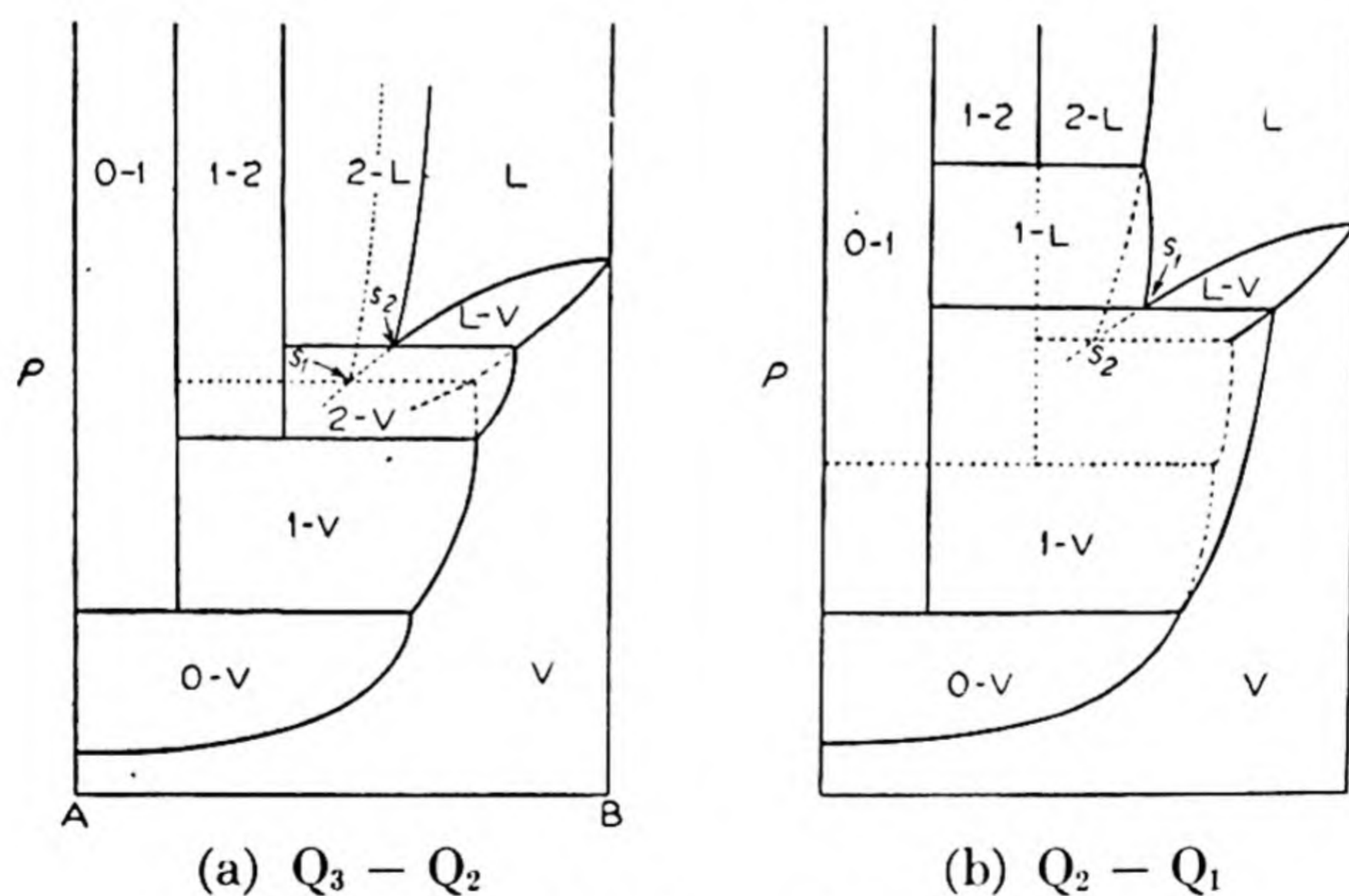


FIG. 7-27. Isotherms of Fig. 7-26.

4. Hydrates

In the system $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ (Fig. 7-28) there is a hydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$) which is always metastable at the vapor pressure of the system. Q_0 is a polymorphic transition point between rhombic and monoclinic anhydrous Na_2SO_4 (or A_R and A_M), of the type discussed in Chapter VI. The stable eutectic E_{10} is the intersection of the ice curve $O_B E_{10}$, the eutectic curve

$A_{10}LB$, the solubility curve of $Na_2SO_4 \cdot 10H_2O$ ($E_{10}Q_{10}$), and the equilibrium $A_{10}VB$. The metastable eutectic E'_7 is on the extension of the ice curve, meeting the solubility curve $E'_7Q'_7$, of $Na_2SO_4 \cdot 7H_2O$, and the equilibria A_7LB and A_7VB , all four being metastable curves. The transition

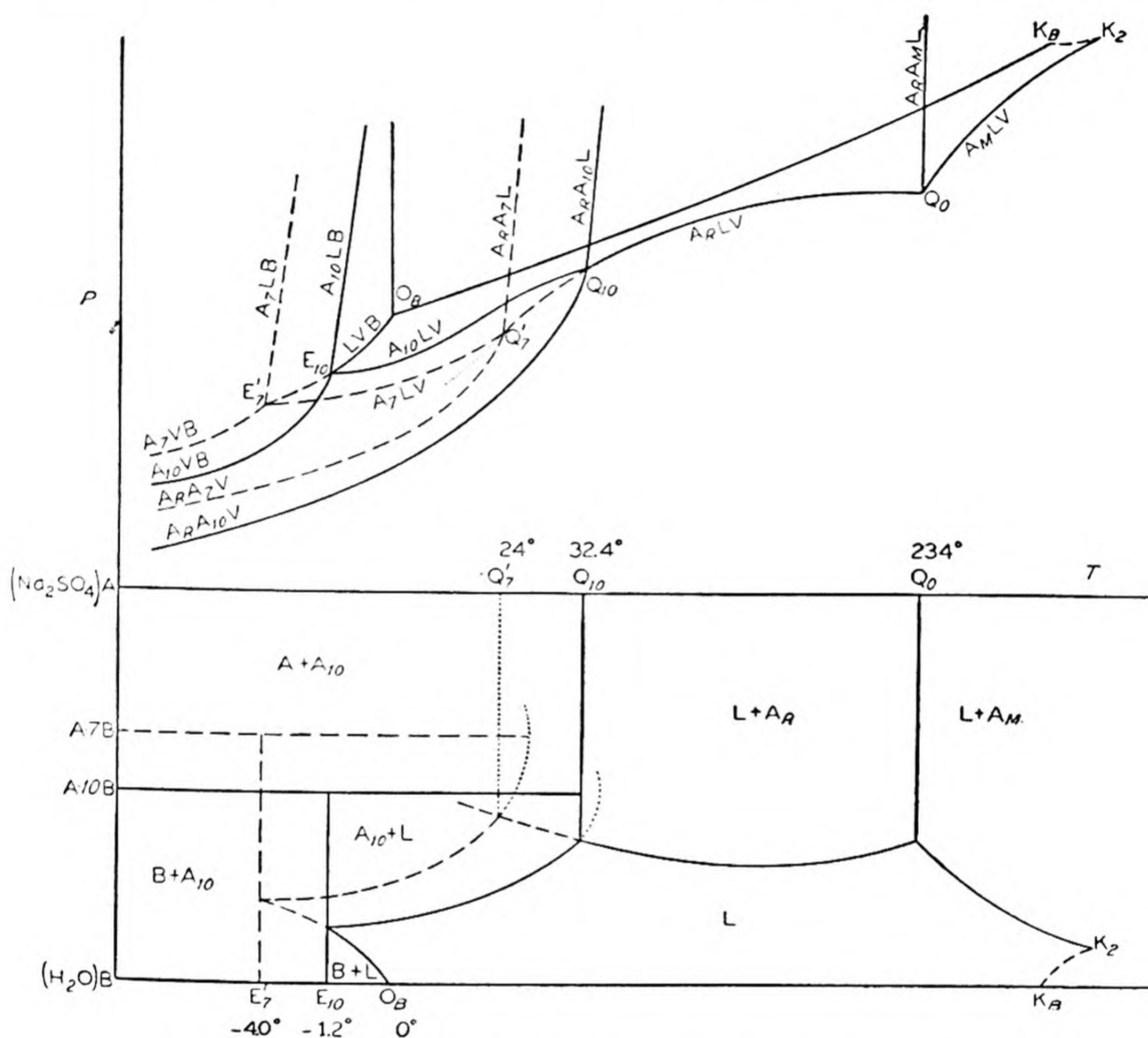


FIG. 7-28. Systems $Na_2SO_4(A)$ -water(B); schematic.

point Q_{10} is the one described in connection with Fig. 7-14;¹⁸ the extension, however, of the solubility curve of rhombic Na_2SO_4 ($Q_{10}-Q_0$) below Q_{10} leads to Q'_7 , the metastable transition point for the phases $Na_2SO_4 \cdot 7H_2O$, $Na_2SO_4(A_R)$, L and V. The point K_2 of Fig. 7-28, the intersection of the solubility curve of monoclinic Na_2SO_4 (A_M) and the critical curve originating at K_B (water) was discussed with Fig. 5-16. An isotherm between O_B

¹⁸ The condensed transition equilibrium $ARA_{10}L$, rising from point Q_{10} , passes through a temperature maximum with increasing pressure, according to G. Tammann, *Z. phys. Chem.*, **46**, 818 (1903). For a similar effect of pressure on the transition temperature of $NaCl \cdot 2H_2O$, see L. H. Adams and R. E. Gibson, *J. Am. Chem. Soc.* **52**, 4252 (1930); the maximum temperature of transition is 25.8° , at 9,500 bars. For the isotherm of the system $NaCl-H_2O$ at 25° , see L. H. Adams, *ibid.*, **53**, 3769 (1931).

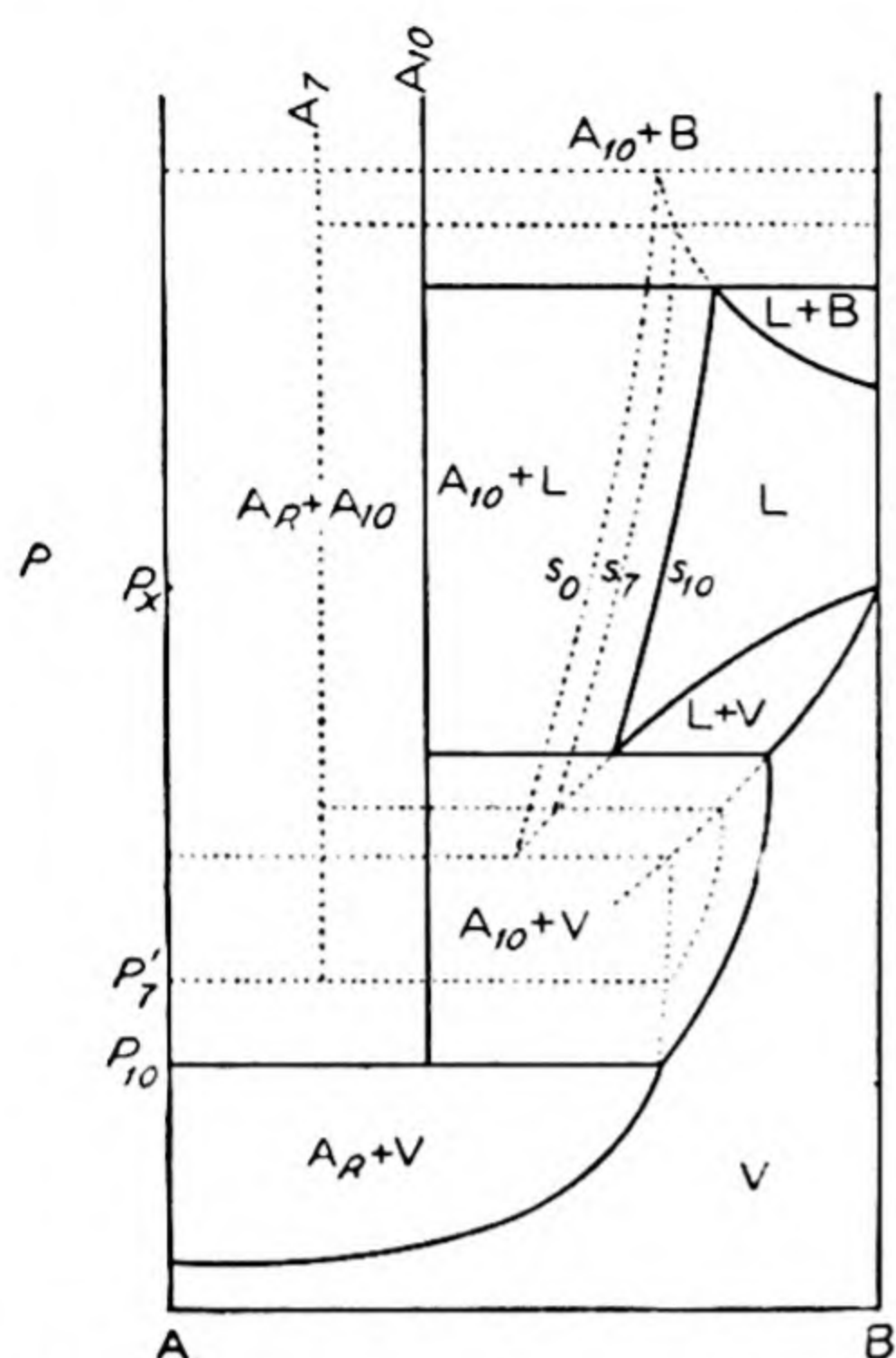


FIG. 7-29. Isotherm of Fig. 7-28, between O_B and Q'_7 .

and Q'_7 is shown in Fig. 7-29. In this diagram it may be seen how the heptahydrate, at the specified T , decomposes at a higher vapor pressure (P'_7) than does the stable hydrate (P_{10}); also that the solubility of the unstable hydrate at any P , such as P_x , at this T , is higher than that of the decahydrate. But furthermore, if the vaporus of the A_R+V equilibrium is extended metastably to intersect the L/V loop, we find, as shown in Fig. 7-28 (the T/c projection) that the solubility s_0 of the anhydrous salt is still higher, since the temperature is below the metastable transition point Q'_7 . Accordingly, as seen in both Fig. 7-28 and Fig. 7-29, the vapor pressure of the solution saturated with the anhydrous salt is lower, at such a temperature, than that of the solution saturated with the heptahydrate,

which is in turn lower than that of the solution saturated with the decahydrate or the stable phase. ("B" in Fig. 7-29 is ice III, as in Fig. 6-18.)

If the three compounds of Fig. 7-26 are the hydrates of $\text{CuSO}_4 \cdot (1, 3, 5\text{H}_2\text{O})$, then the isotherm at 25° , which is between O_B and Q_3 , is that of Fig. 7-30,¹⁹ in which again the vaporus is omitted. (A tetrahydrate has also been reported on the basis of thermal analysis of open air systems not involving the liquid phase,²⁰ although such a hydrate has never been reported in equilibrium with liquid solution. The observations would be consistent if the plane of the tetrahydrate were cut off by the decomposition $4 \rightleftharpoons 5 + 3$, at a quadruple point of the type of Q' of Fig. 7-24(a), before it reaches an equilibrium with L at the pressure of the system. At any rate, the tetrahydrate is regularly missed in usual studies, even not involving a liquid phase, and the present discussion therefore ignores it.)

With the successive formation of a series of hydrates, such a diagram (Fig. 7-30) has a characteristic step-wise appearance, in which each horizontal marks the pressure required for the formation of a higher hydrate or for its decomposition. No water is taken up by the anhydrous CuSO_4 at this T , until P (that is, the partial pressure of water vapor) rises to 0.8 mm,

¹⁹ For the pressures in Fig. 7-30, see H. W. Foote and S. R. Scholes, *J. Am. Chem. Soc.*, **33**, 1309 (1911); R. E. Wilson, *ibid.*, **43**, 704 (1921); A. A. Noyes and L. R. Westbrook, *ibid.*, **43**, 726 (1921); C. D. Carpenter and E. R. Jette, *ibid.*, **45**, 578 (1923); E. M. Collins and A. W. C. Menzies, *J. Phys. Chem.*, **40**, 379 (1936).

²⁰ T. I. Taylor and H. P. Klug, *J. Chem. Physics*, **4**, 601 (1936).

which is the pressure for the equilibrium $1 \rightleftharpoons 0 + V$, or the decomposition pressure of the monohydrate. The pressure is then constant, at 0.8 mm, until formation of the monohydrate is complete. Then again no water is taken up until the pressure rises to 5.6 mm, the decomposition pressure of the trihydrate in the equilibrium $3 \rightleftharpoons 1 + V$. Finally, above the decomposition pressure of the pentahydrate (7.8 mm, for the equilibrium $5 \rightleftharpoons 3 + V$), water is again not taken up until the deliquescence pressure

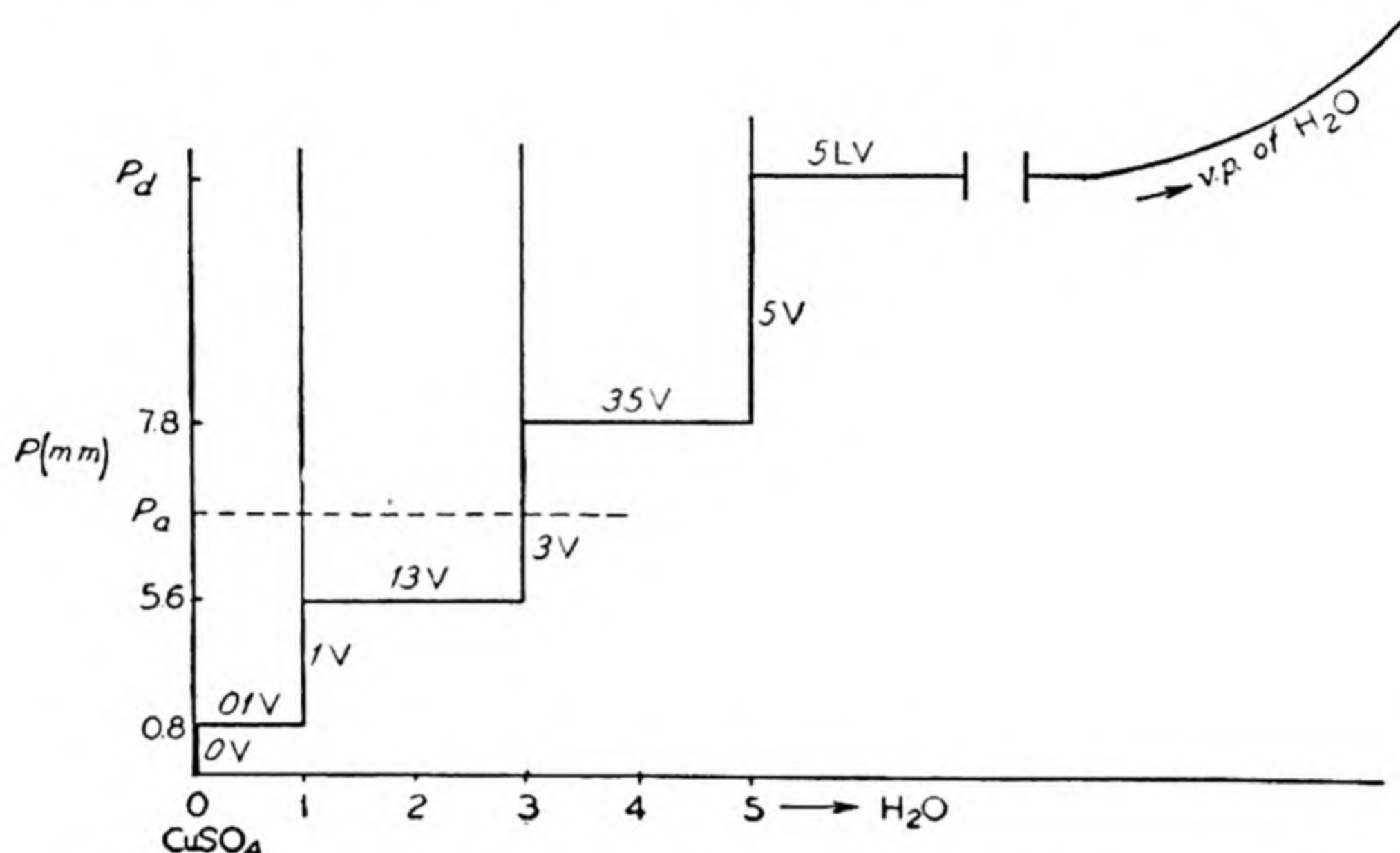


FIG. 7-30. Isotherm of Fig. 7-26, between O_B and Q_3 ; schematically, the 25° isotherm of the system $\text{CuSO}_4(\text{A})$ -water(B).

For the abscissa: Moles H_2O per mole CuSO_4 in condensed phases.

P_d is reached, for the formation of the saturated solution of the pentahydrate, beyond which the relations are those already discussed in Fig. 5-19(b). If CuSO_4 and water are allowed to come to equilibrium at 25°, the final equilibrium state is defined by this diagram, for any specified final equilibrium vapor pressure. If the vapor pressure is fixed at any value between 5.6 and 7.8 mm, the final solid will be the single phase $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$. A hydrate, meaning here an incongruently vaporizing hydrate, a true *binary* compound, does not have a vapor pressure at a specified T but a decomposition pressure; and for the trihydrate, this is 5.6 mm at 25°. If the P is < 5.6 mm the trihydrate decomposes; if > 7.8 mm, the decomposition pressure of the pentahydrate, it forms the pentahydrate.

If P_a is the aqueous pressure of the atmosphere, this figure also means that the hydrates 1 and 3, with decomposition pressures $< P_a$, will not lose water in the open air at this temperature, although both the anhydrous salt and the monohydrate will take on water to form the trihydrate, while the pentahydrate, with decomposition pressure $> P_a$, will “effloresce” in the

air, leaving the trihydrate. Similarly, in this case, any solution will evaporate in the open, to leave first the pentahydrate and finally the trihydrate. A particular hydrate is therefore stable in air (or in any atmosphere of given aqueous pressure) at a given T , only if the prevailing aqueous pressure is greater than its decomposition pressure at that T (in respect to formation of a lower hydrate or of the anhydrous form) and smaller than the decomposition pressure of the next higher hydrate and the vapor pressure of its saturated solution.

The pressure, at constant T , then will have a fixed value only when the vapor is in equilibrium with a mixture of two phases, and this is a convenient way of maintaining a constant vapor pressure (hygrostats). A large quantity of anhydrous CuSO_4 will prevent the aqueous pressure in a system from rising above 0.8 mm (at 25°), since the system $01V$ is isothermally invariant. A large quantity of the monohydrate will prevent the vapor pressure from falling below 0.8 mm, its decomposition pressure; and it may also be used to prevent the vapor pressure from rising above 5.6 mm, the pressure of the system $13V$. An anhydrous solid, such as BaO , forming a hydrate of extremely low decomposition pressure, will therefore be a powerful desiccant, the system $01V$ being a hygrostat of very low aqueous pressure.

5. Solid Solution in the Equilibrium Solid-Vapor

In an isothermal diagram such as Fig. 7-30 for the reaction of gas and solid, the solid composition (solidus line) is a vertical line while no gas is being absorbed (single, pure, solid phase), and a horizontal if the solid consists of a mixture of two solid phases. If the solidus is a curve, the composition increasing with P , then the gas is being absorbed to form a (variable) solid solution. This may involve direct penetration of the solid crystal lattice by the vapor, as presumably in the zeolites \pm water; or it may be explained as the formation of a solid compound which then forms a solid solution with the original solid phase. This seems to be the case, for example, in the system $\text{AgCl}-\text{NH}_3$ ²¹ above 33° , between the compounds $\text{AgCl}\cdot\text{NH}_3 (= C_1)$ and $2\text{AgCl}\cdot 3\text{NH}_3 (= C_2)$; schematically, the isotherm would have the appearance of Fig. 7-31, in which, moreover, C_3 represents the compound $\text{AgCl}\cdot 3\text{NH}_3$. When all the AgCl has been transformed, at such a temperature, to the compound C_1 , this no longer remains pure but begins at once to absorb NH_3 to form a solid solution, S_1 , which may be considered a solid solution of compound C_2 in C_1 . The mutual solubility of the two compounds, however, is not unlimited, and, when the concentration x is reached, a second, conjugate solid solution S_2 of composition y

²¹ W. Biltz and W. Stollenwerk, *Z. anorg. Chem.*, **114**, 174 (1920).

appears, presumably C_1 in C_2 ; and with two solid phases now present the system is isothermally invariant. But the relative amounts of x and y , both of fixed composition, will change as NH_3 is absorbed, until only y is left. This then varies continuously with pressure, on further absorption of NH_3 , until it reaches the composition C_2 . Beyond this point the relations are again as in Fig. 7-30.²² Schematically, with the vaporus included, the relations are those of Fig. 7-32. The miscibility gap between S_1 and S_2 may or may not close with increasing P , with a critical solution point at K .

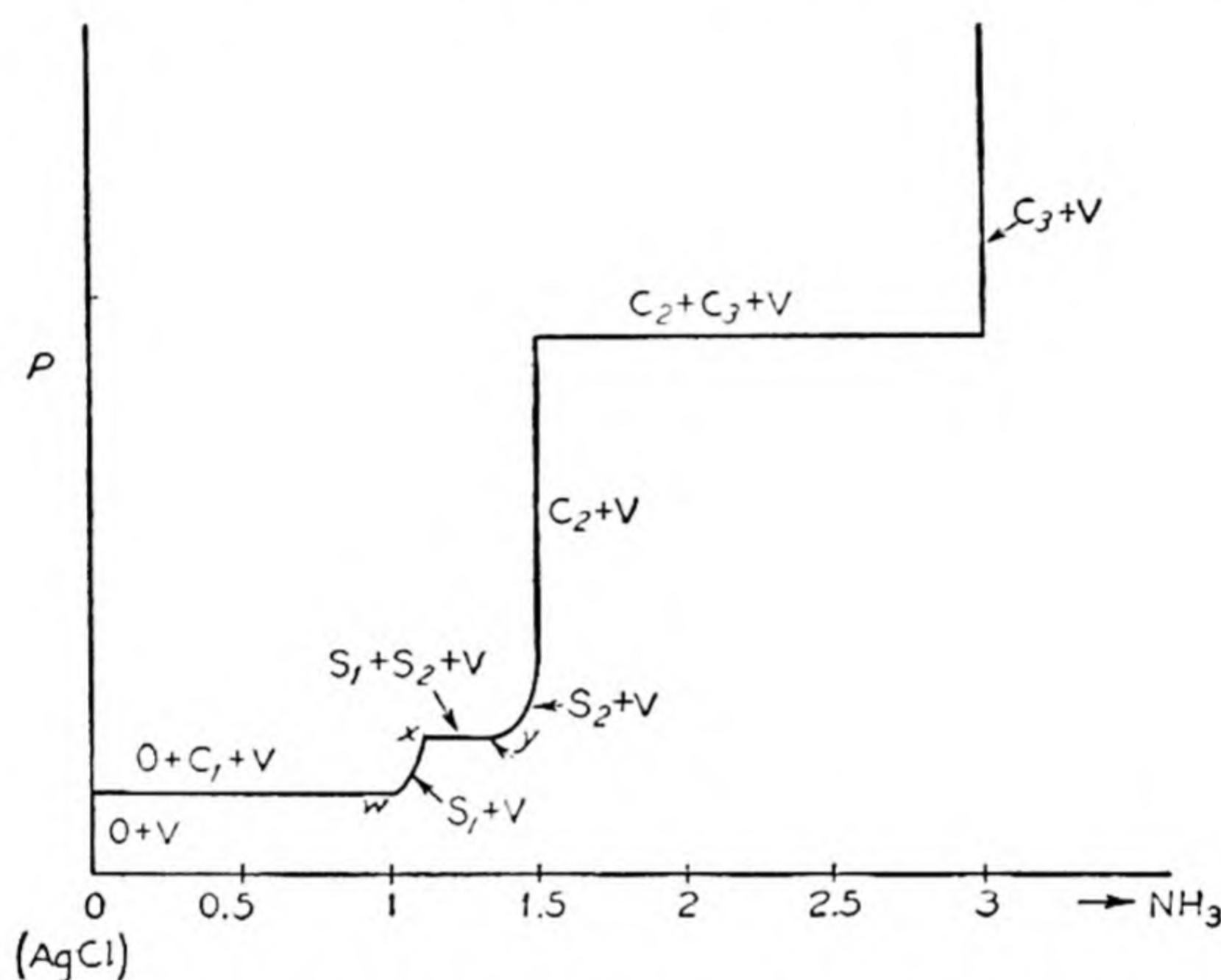


FIG. 7-31. Isotherm (above 33°) of system AgCl-NH_3 (schematic).

Abscissa: Moles NH_3 per mole AgCl in condensed phases.

Such behavior, with solid solution formation between adjacent compounds, is not uncommon in solid-gas systems; it may also occur in systems of metallic oxides and CO_2 , or of metals and oxygen.

In the system palladium-hydrogen, the hydrogen is absorbed directly by the metal forming a solid solution based on the metal itself. The solidus of each isotherm is of the shape shown schematically as $wxyz$ in Fig. 7-32, with an intermediate region of isothermal invariance indicating a discontinuity of the solid solution. Isotherms from 200° to 313° have been determined, and when the breaks in these isotherms (points x, y) are plotted we

²² According to Biltz and Stollenwerk, *loc. cit.*, who present an isotherm at 42° , the solid phase x is pure $\text{AgCl} \cdot \text{NH}_3$, or C_1 , whereupon the section wx of Fig. 7-31 should be vertical. The actual data, however, are not sufficient to rule out some solid solution of the sesqui-ammine in the mono-ammine. The system AgBr-NH_3 involves the same compounds, with limited solid solution between the first two. In the system AgI-NH_3 , with the compounds $\text{AgI} \cdot (0.5, 1, 1.5, 2, 3) \text{NH}_3$, similar solid solution was observed between pure AgI and the hemi-ammine, and between the sesqui- and the di-ammines.

have an outline of the *MG* on *P/c* projection (Fig. 7-33). The outline, we may say, is somewhat hazy, but it nevertheless raises interesting possibilities concerning the formation of definite compounds. The *MG* is closed above

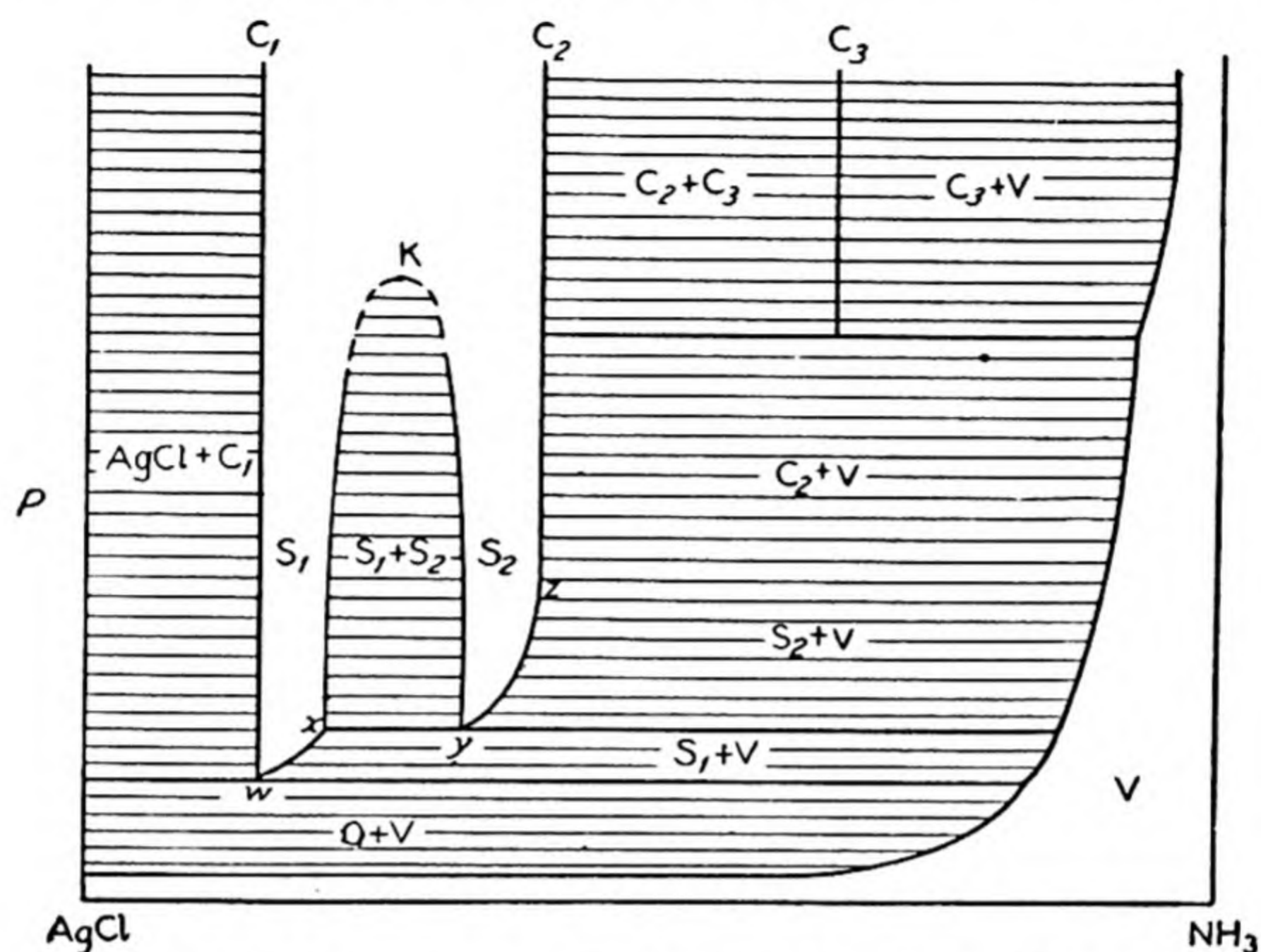


FIG. 7-32. Schematic $(P/c)_T$ relations for Fig. 7-31.

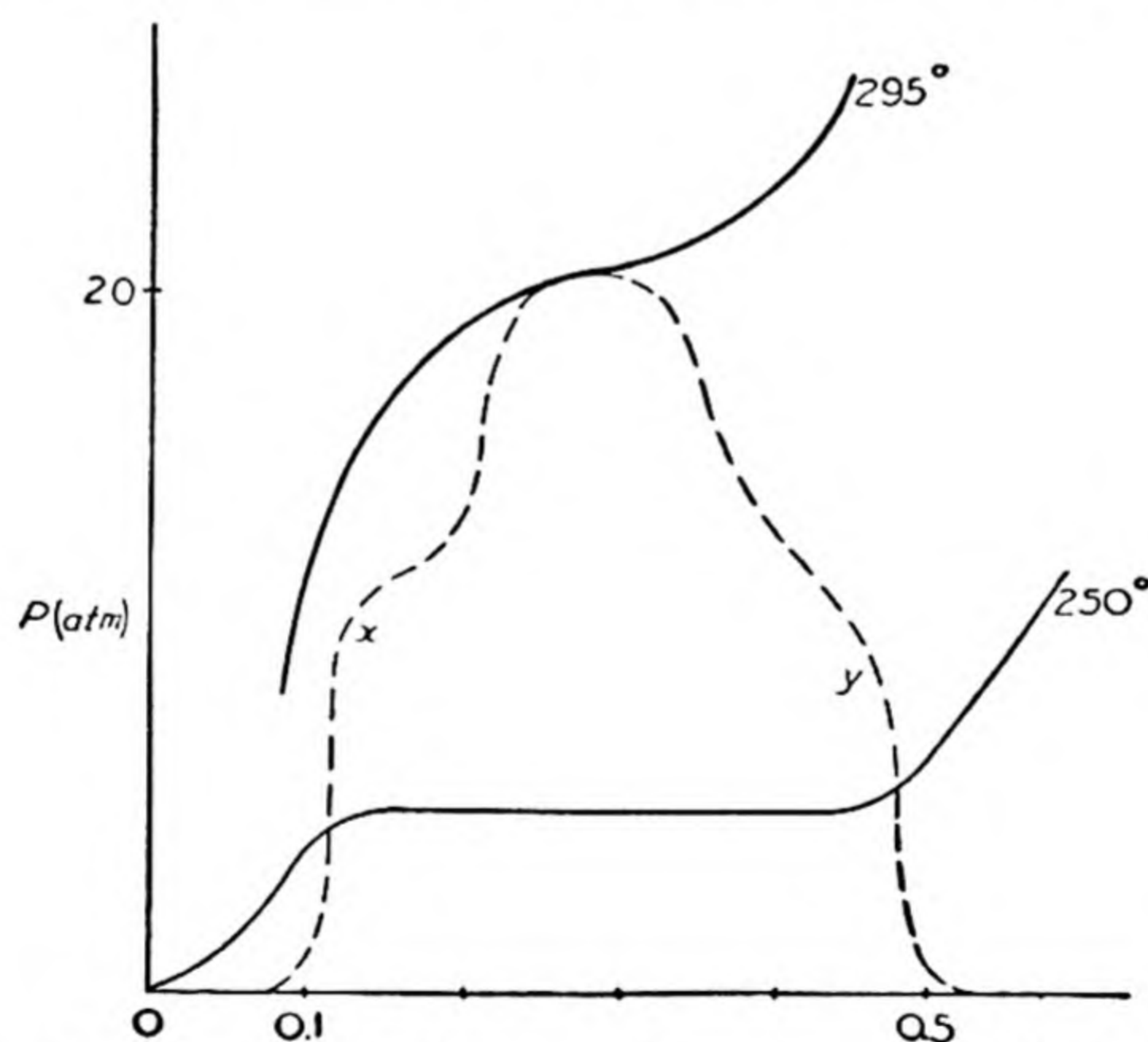


FIG. 7-33. Schematic isotherms of system palladium-hydrogen.
Abscissa: Atomic ratio, H/Pd, in solids.

295°; but its walls, which are the compositions of limiting or conjugate solid solutions, have regions in which this limiting composition seems to be independent of *P* and *T*, particularly the walls at lower *P* and *T*, with atomic ratios close to the formulas Pd_8H and Pd_2H .²³ Near the closed end of the gap there are indications, less distinct, of constancy of composition at Pd_4H

²³ L. J. Gillespie and L. S. Galdstaun, *J. Am. Chem. Soc.*, **58**, 2565 (1936).

and Pd_3H . Roughly the same relations are observed in the system palladium–deuterium.²⁴

D. Compound with Congruent Melting Point

Although a compound melting incongruently at the vapor pressure of the system may reach congruent melting relations at high pressure, “a congruently melting compound” conventionally means one melting congruently at the vapor pressure of the system. This means that the congruent melting curve ($C = L$), a 2-phase equilibrium of restricted univariance, meets, as the pressure is lowered, the L/V loop of the binary system at a singular point M , called *the* congruent melting point, involving the three phases C, L, V — C and L having the same composition.

The melting point or solubility surface of the compound in the space model is generated by the curve $e_1T_c(\text{or } P_c)e_2$ of Fig. 7-3; this surface has a rounded edge of congruent melting, as seen in Fig. 7-4, the projection of which on a P/T face is the congruent melting curve $C = L$, which we shall assume to have a positive P/T slope. This surface always has a temperature maximum (T_c) at any given pressure. Also, the L/V loop, if of the ascendant type, rises at any given T from A to B in respect to P ; if there is a P_{min} in the L/V loop, as is probable with compound formation, this minimum will be close to pure A if A is the relatively non-volatile component, and the loop will still rise in general from near A to pure B. Hence it will be seen that when the melting point surface of the compound meets the L/V loop, the outline of their intersection from E_1 to E_2 , shown in projections in Fig. 7-34, may or may not have a pressure maximum, P_m , but must always have a temperature maximum, T_m . This intersection curve involves the three phases C, L, V, and since the order of the composition of these phases is not the same throughout the curve from E_1 to E_2 , we shall use the indifferent term **intersection curve** for it as a whole. Somewhere on this intersection curve there will be a singular point, type m , representing the intersection of the congruence curve (the rounded edge of the melting surface of C) with the L surface of the L/V loop, at M , the congruent melting point. Consideration again of the shapes and slopes of the two surfaces intersecting on the curve E_1E_2 shows that M must lie, as in Fig. 7-34, between the temperature maximum T_m and the point E_1 , on the A side of the intersection curve.

(With the L/V loop rising, with respect to P , from A to B, T_m will be on the B side of C (and hence of M) if the congruent fusion curve of the compound ($C = L$) has a positive P/T slope; it will be at C, and therefore

²⁴ L. J. Gillespie and W. R. Downs, *ibid.*, 61, 2496 (1939).

identical with M , if this fusion curve is vertical in P/T ; and it will be on the A side of C or of M if the fusion curve of the compound has a negative P/T slope.)

Point E_2 (Fig. 7-34) is now a 4-phase, invariant, eutectic point, involving CLVB; the order L-V is fixed because the L/V loop is assumed ascendant, in P/c , from A to B, at least in this region. Point E_1 involves the four phases ALCV. It is the intersection of the following four curves: the solubility curve of A, ALV (this being the order near E_1 , although the order may

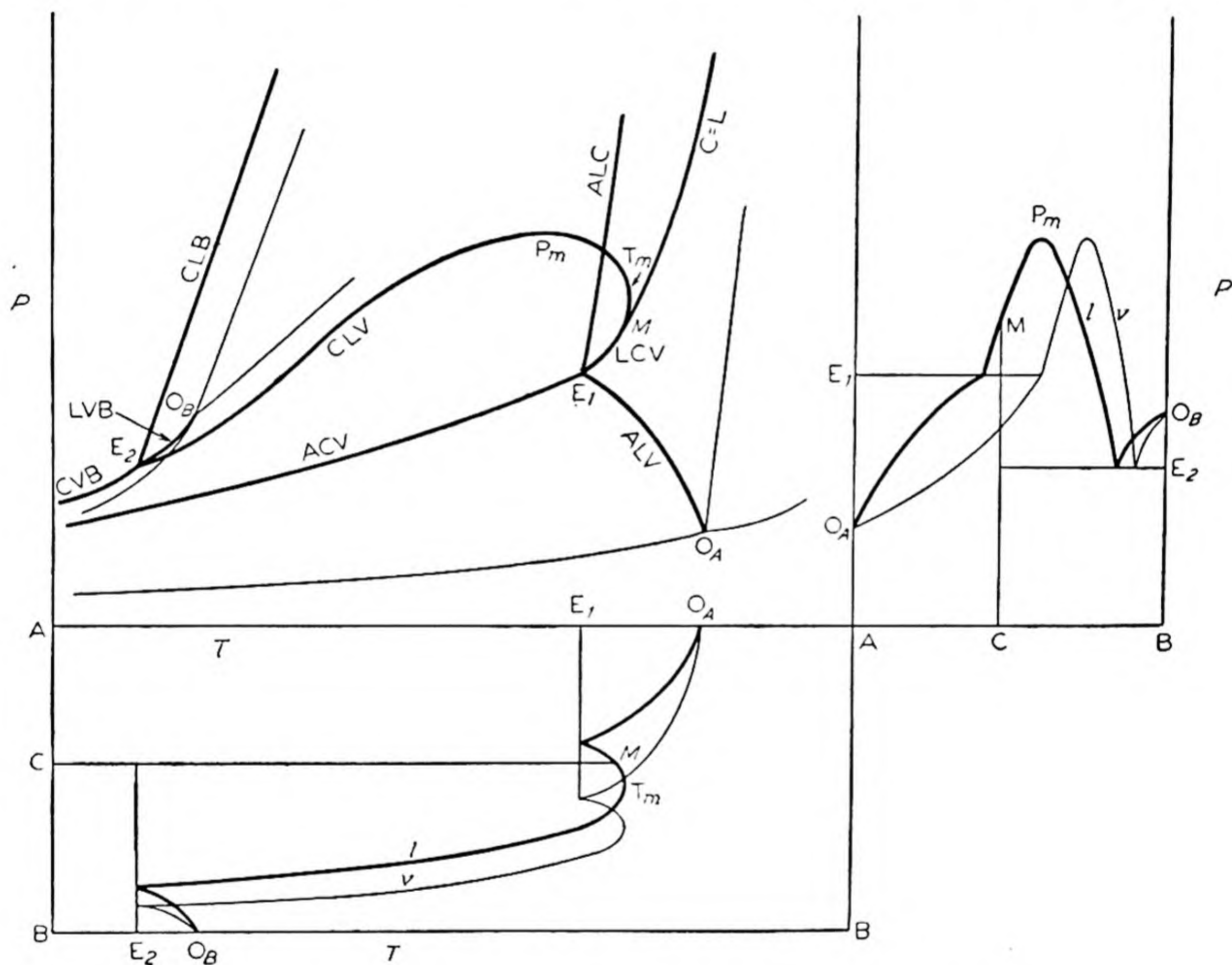


FIG. 7-34. Compound with congruent melting point.

become AVL if the curve crosses a pressure minimum of the L/V loop between E_1 and O_A); the condensed "eutectic curve," rising above E_1 , ALC; the decomposition or incongruent vaporization curve of C, ACV, approaching E_1 from low T and P ; and the intersection curve coming from M , the congruent melting point. Because of the order of the phases on the incongruent vaporization curve ACV, the point E_1 , with the order ALCV, may be called an "incongruent eutectic point"; it is not altogether comparable to a "congruent eutectic" such as E_2 , in which both L and V lie between the two solids in composition. In the P/c and T/c projections of Fig. 7-34 the composition of the vapor at E_1 is shown between C and the

liquidus from E_2 to M , but it may also lie between this liquidus and pure B, anywhere, that is, between C and B.

It follows also, now, that that part of the intersection curve from E_1 to M involves the phases (and order) LCV, while the rest of the intersection curve, E_2 to M , involves CLV. This means that, whereas both are solubility curves in the broad sense defined in Chapter III, it will be clearer and more informative here to distinguish the branch E_2M as the *solubility curve* of the compound at the pressure of the system, and E_1M as a *decomposition curve*, for the 3-phase univariant reaction $C \rightleftharpoons L + V$. Despite this distinction, which is important for the understanding of the relations, the curve E_1E_2 is continuous and smooth through M .

Finally, therefore, the plane of C is in this case (considered open at high P and low T) bounded by the congruent melting curve $C = L$ down to point M , its congruent melting point, by the decomposition curve LCV from M to E_1 , the incongruent eutectic with A, and by the decomposition curve ACV on the left of and below E_1 . The congruent curve $C = L$ is tangent in P/T projection to the intersection curve at point M , whether M is on the B or the A side of T_m .

Further elucidation is given by the isotherms and isobars of Figs. 7-35 and 7-36, which should now be self-explanatory. These diagrams are schematic, and, although set side by side for comparison, they do not necessarily indicate the relative pressures from one isotherm to the next or the relative temperatures from one isobar to the next; this defect is rendered necessary for the sake of clarity. The isotherms preceding those of Fig. 7-35 are not shown, since they would be schematically those of Fig. 7-15(a) at $T < E_2$, 7-15(b) between E_2 and O_B , and 7-15(c) between O_B and E_1 .

P_m , the pressure maximum of the solubility curve of the compound (Fig. 7-36(b)), marks the appearance of the CLV (solubility) curve on decrease of P ; since P_m is a maximum, two sets of 3-phase tie-lines for the equilibrium CLV appear as P falls through P_m (Fig. 7-36(c)), the lower tie-line being the portion P_mE_2 proceeding normally to the eutectic E_2 , the upper proceeding toward M , the congruent melting point. Similarly in the isothermal sections, the temperature maximum T_m (Fig. 7-35(d)) is the first contact, with falling T , of the L/V loop with the melting surface of C, and gives rise to two portions of the solubility curve CLV (the two tie-lines CLV appearing on Fig. 7-35(c) as T falls below T_m); again one portion, now the upper tie-line, proceeds to the eutectic E_2 , the other, the lower tie-line, toward M .

When the point M is reached, a singular point with particular values of P , T , and phase compositions in three phases with the restriction that solid and liquid have the same composition — we have the sections 7-35(b) and

7-36(d). The point M marks the upper limit of the decomposition equilibrium LCV, which then appears as a tie-line at lower T , in Fig. 7-35(a), and lower P , in Fig. 7-36(e). This decomposition curve then ends at E_1 , between 7-35(a) and 7-15(c) and between 7-36(e) and (f), to be replaced by the incongruent vaporization curve ACV.

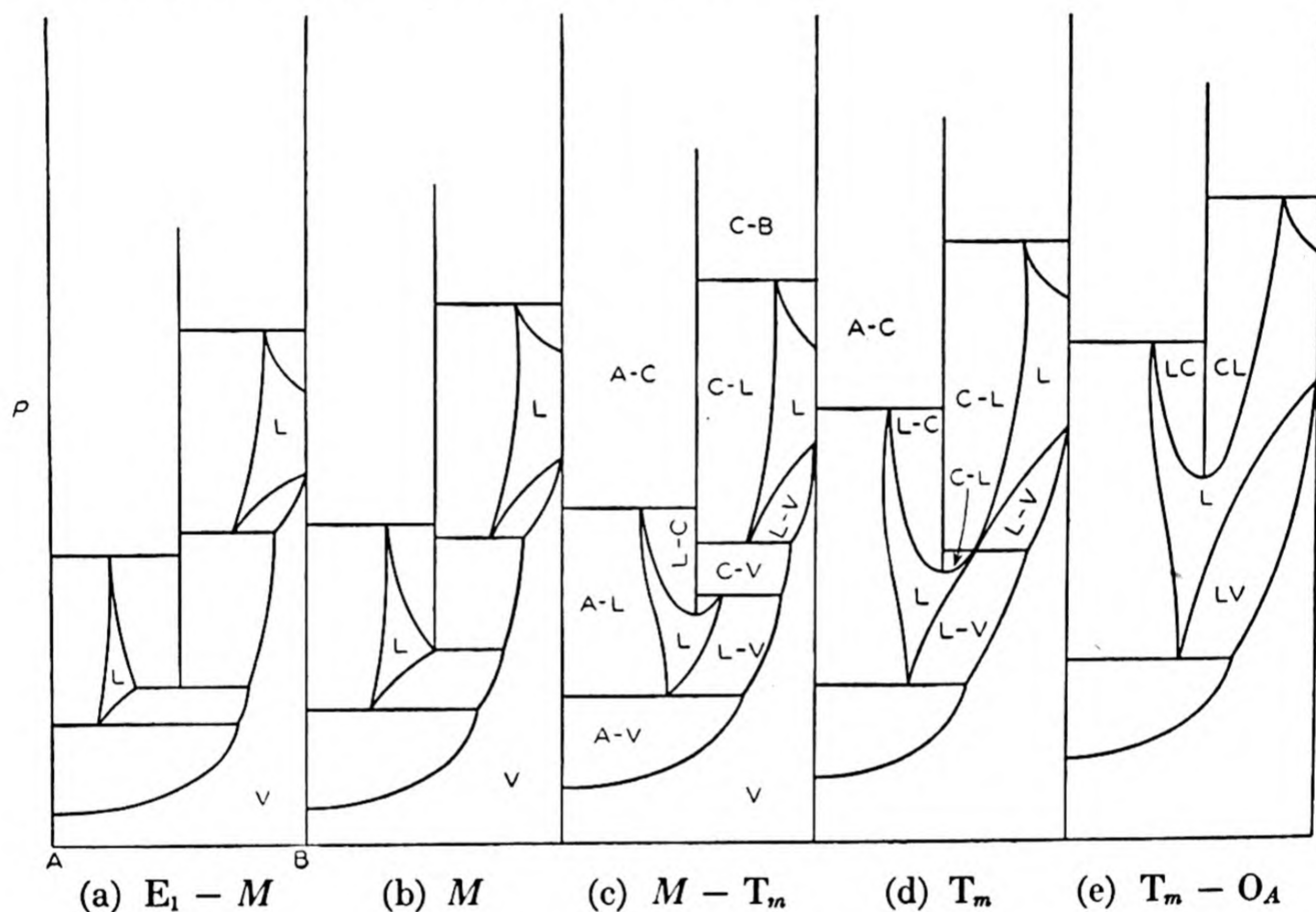


FIG. 7-35. Isotherms of Fig. 7-34.

The variance of the point M was discussed in Chapter I, in connection with "equality restrictions"; it has no degrees of freedom, in the sense that it is a singular point (type m) of the space model. But it is not physically invariant, since it has only three phases and they are not all of the same composition. If the pure compound is heated as a single phase in a closed vessel of variable volume at constant P , ($P > P_M$), it melts at constant T . But it does not have either a constant melting point or a constant transition point at the vapor pressure of the system, or with a vapor phase present, since there will be only three phases present and, as vapor is produced at the expense of the other two phases, the composition of the liquid changes and hence also the pressure and the temperature. In the open air, then, it can give only an approximately constant melting point, depending on the extent of vaporization. If complexes consisting of the three phases C, L, V, or equilibrium mixtures on the curve E_1E_2 , under the pressure of the system, are heated, they do not halt at the point M with invariance. In all cases

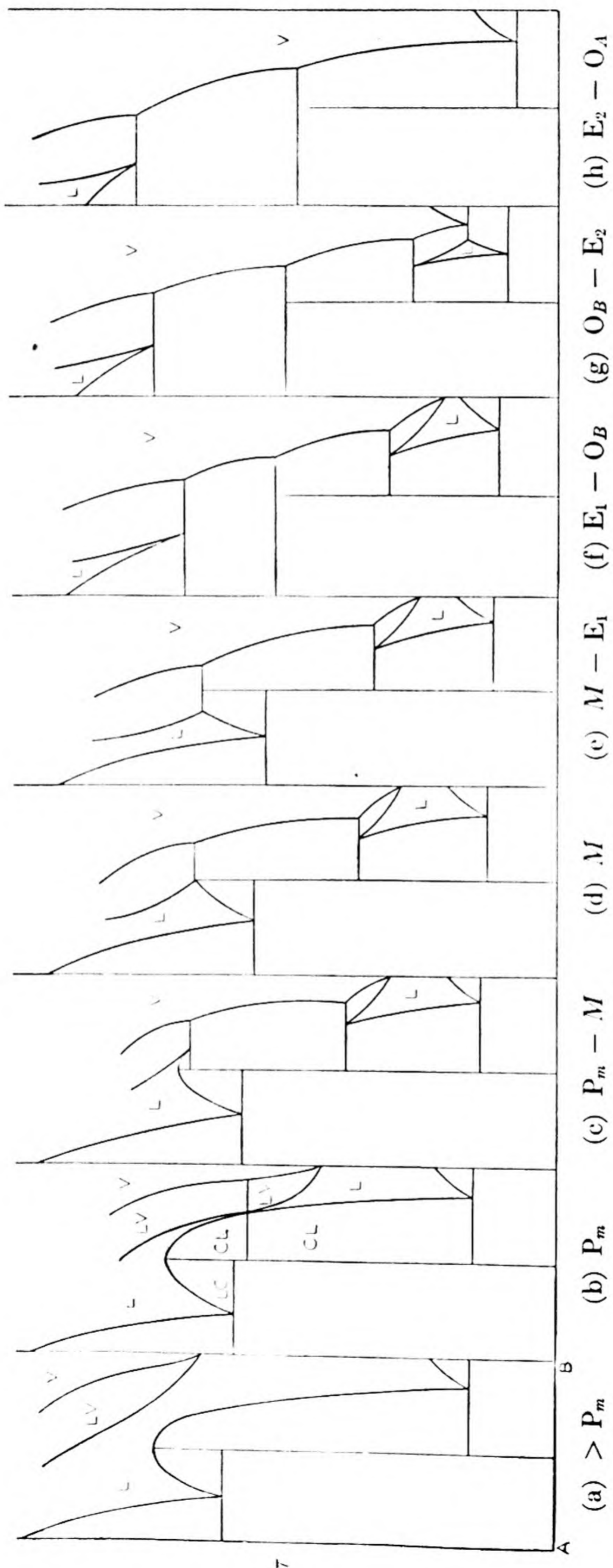


FIG. 7-36. Isobars of Fig. 7-34.

the transition involves the univariant disappearance of the solid phase to leave, at some temperature below T_m , a bivariant system consisting of L and V, phases of different compositions. If the mixture starts on the curve E_1M , with its total composition on the A side of C, the solid phase is lost before the temperature of M is reached, while if the total composition is on the B side of C the temperature may go beyond M , toward T_m , before the solid is consumed.

Strictly speaking, then, the maximum of the freezing point curve of the compound occurs at the composition of the compound only if the equilibrium does not involve the vapor. The open air freezing point diagram, in which the vapor phase is always present, will theoretically have a maximum melting point on the E_1E_2 curve, on the B side of the composition of the compound for the relations chosen in Fig. 7-34. The freezing point diagram may be determined in the open as long as the atmospheric pressure is greater than the vapor pressure of the system on the curves $O_AE_1E_2O_B$, but it is not simply an isobar of the binary system above the pressure of these curves. It is still the projection of an intersection curve, that is, the intersection of the three solubility surfaces of A, C, and B with the L/V loop. The whole intersection diagram will be slightly affected by the air and its pressure, being now a 3-dimensional curve in the isobaric space model of a ternary system (if air is counted as one component), and its projection on a T/c plane, in which the concentration of the air is not plotted (c being merely the proportions of A and B), still preserves the features of the T/c projection of Fig. 7-34, with T_m on the B side of C.

The maximum melting point in Figs. 7-36(a, b, c), then, is at the composition C only if these are true binary isobars, whereas if they represent open air relations at constant total gas pressure of 1 atm, this maximum must lie slightly on the B side of C.

(Let it be noted that all this refers to a true *binary* compound in the sense defined at the beginning of this chapter. If the compound has a triple point with $C = L = V$ in composition, then the maximum melting point of C in the "system" A-B is at the composition C whether or not vapor is present, and hence whether or not the system is open to the air. This maximum, however, is no longer a "congruent melting point" in the sense of a relation in a binary system, but simply the melting point of the compound as a unary system, its triple point with vapor present. If, moreover, the "system" A-B is now plotted as a "binary" system, this maximum is no longer rounded, but actually the intersection of two curves, one for the solubility of C in the system A-C, the other for the solubility of C in the system C-B, as seen in the T/c projection of Fig. 7-37, which is simply the juxtaposition of two independent binary systems.)²⁵

²⁵ The 1:1 compound of pyridine and methyl iodide gives such a pointed maximum in the freezing point diagram; A. H. W. Aten, *Z. phys. Chem.*, 54, 124 (1906).

As open air diagrams, these three figures, 7-36(a, b, c), show, moreover, that, if P_a (the atmospheric pressure) is $> P_m$, only unsaturated solutions reach a boiling point. If $P_a < P_m$, with P_a as in Fig. 7-36(c), we may have the boiling of solutions saturated with the compound, and the relations would be essentially as already discussed in Chapter V, Figs. 5-11 to 5-15, except that we would be dealing with the precipitation of the compound rather than of a pure component. The same is true, of course, for the case of incongruently melting compounds; in a case like Fig. 7-14 only unsaturated solutions would reach the boiling point since the vapor pressure on the solubility curves (of C and of A) drops steadily from E to O_A . But in Fig. 7-26, if P_a is between Q_3 and Q_2 (the transition points of the hydrates C_3 and C_2 , let us say), then unsaturated solutions, increasing in concentration, in respect to the non-volatile salt A, on boiling, would reach the solubility curve 2LV of the hydrate C_2 and boil with isobaric invariance, leaving the hydrate as sole phase. The temperature would then rise, but the hydrate would theoretically undergo no decomposition until the decomposition curve 12V is reached, when it decomposes at constant temperature — all provided that the hydrate may be assumed to be surrounded by water vapor at atmospheric pressure, as it was during the boiling of the solution. What actually happens in such an experiment in the open, however, is that, as soon as the liquid has disappeared, the water vapor is replaced by air and the partial pressure of water (component B) drops at once, so that at the high temperature which has been reached the hydrate begins immediately to decompose, and it is generally no longer an equilibrium system. Approximately, from then on, the experiment may be considered isobaric at the partial pressure of H_2O (B) of the air.

Fig. 7-38 shows, in schematic P/T projection, part of the system $Zn(NO_3)_2-H_2O$, with three congruently melting hydrates.^{26, 27} The curve 6LV is the intersection curve of the hexahydrate, rising from the eutectic with ice, E_2 , and, after passing through both a P -maximum and a T -maximum, ending at E_1 , the incongruent eutectic with the tetrahydrate. The

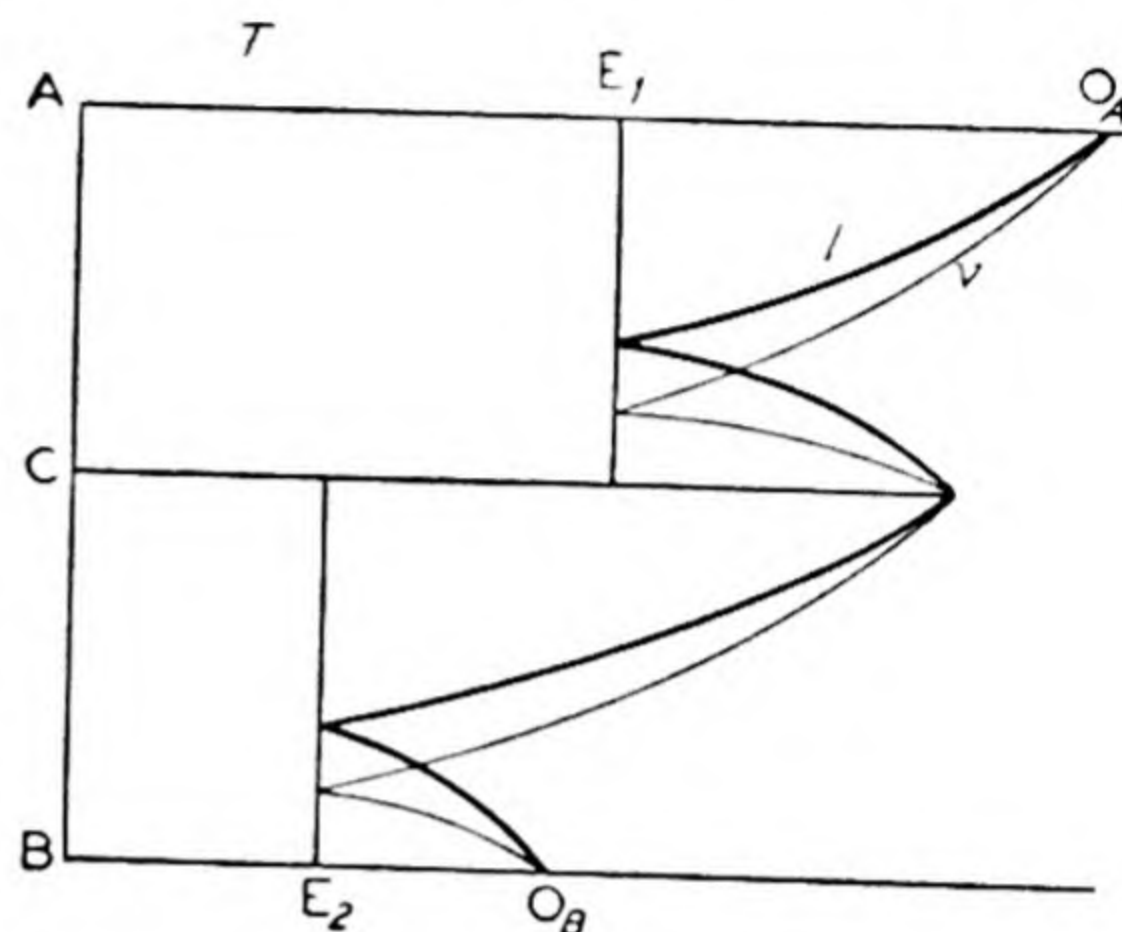


FIG. 7-37. T/c projection for compound with triple point.

²⁶ W. W. Ewing and H. M. Fisher, *J. Am. Chem. Soc.*, **59**, 1046 (1937).

²⁷ Another similar and interesting example is the system iodine-chlorine, forming the congruently melting compounds $ICl(\alpha-ICl \text{ stable}, \beta-ICl \text{ always metastable})$ and ICl_3 ; W. Stortenbeker, *Z. phys. Chem.*, **3**, 11 (1899).

curves 4LV and 2LV are the similar intersection curves of the tetra- and dihydrates. The last, incomplete, curve is the solubility curve of the monohydrate.

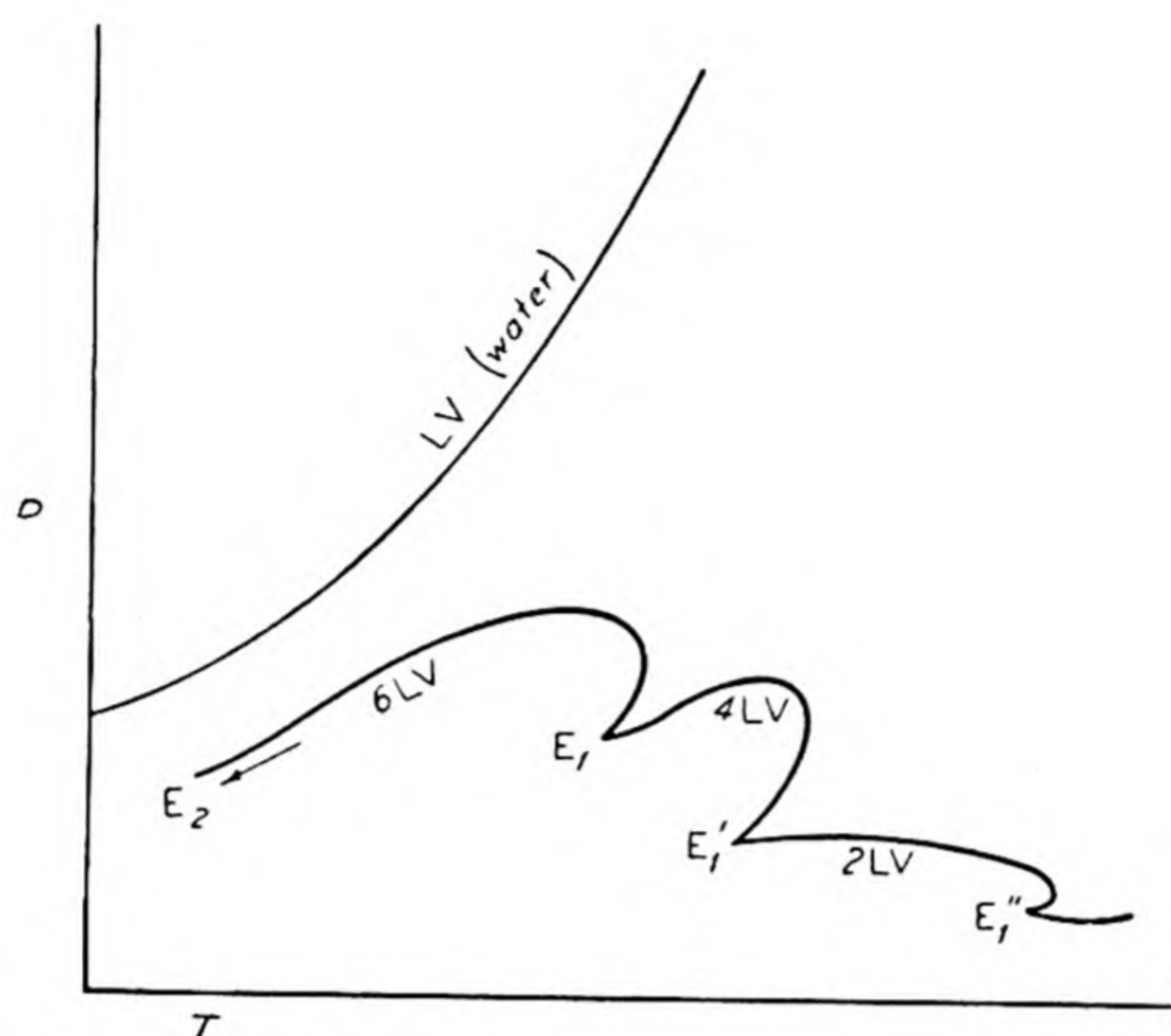


FIG. 7-38. Portion of system $\text{Zn}(\text{NO}_3)_2\text{-H}_2\text{O}$ (schematic).

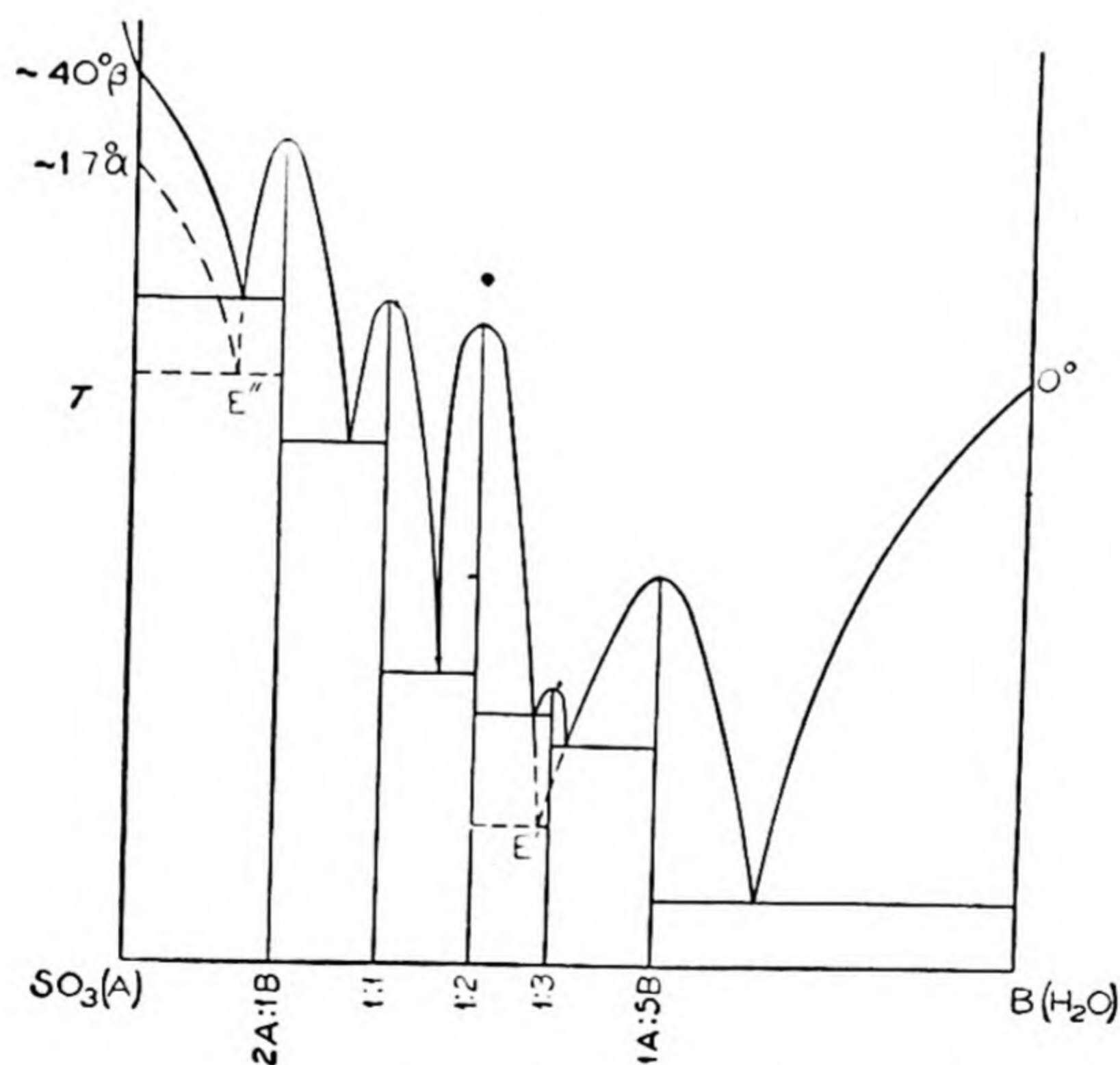


FIG. 7-39. System $\text{SO}_3\text{-H}_2\text{O}$ (schematic); see Footnote 28.

E. Examples

Some examples of systems ("condensed" diagrams) with a number of compounds, both congruently and incongruently melting, are given in the following figures. Fig. 7-39 is the freezing point diagram (schematic) of the

system $\text{SO}_3\text{-H}_2\text{O}$, with five congruently melting hydrates.²⁸ On supercooling in respect to the compound 1:3, the 1:2 and the 1:5 compounds give a metastable eutectic as indicated at E' . With two polymorphic forms

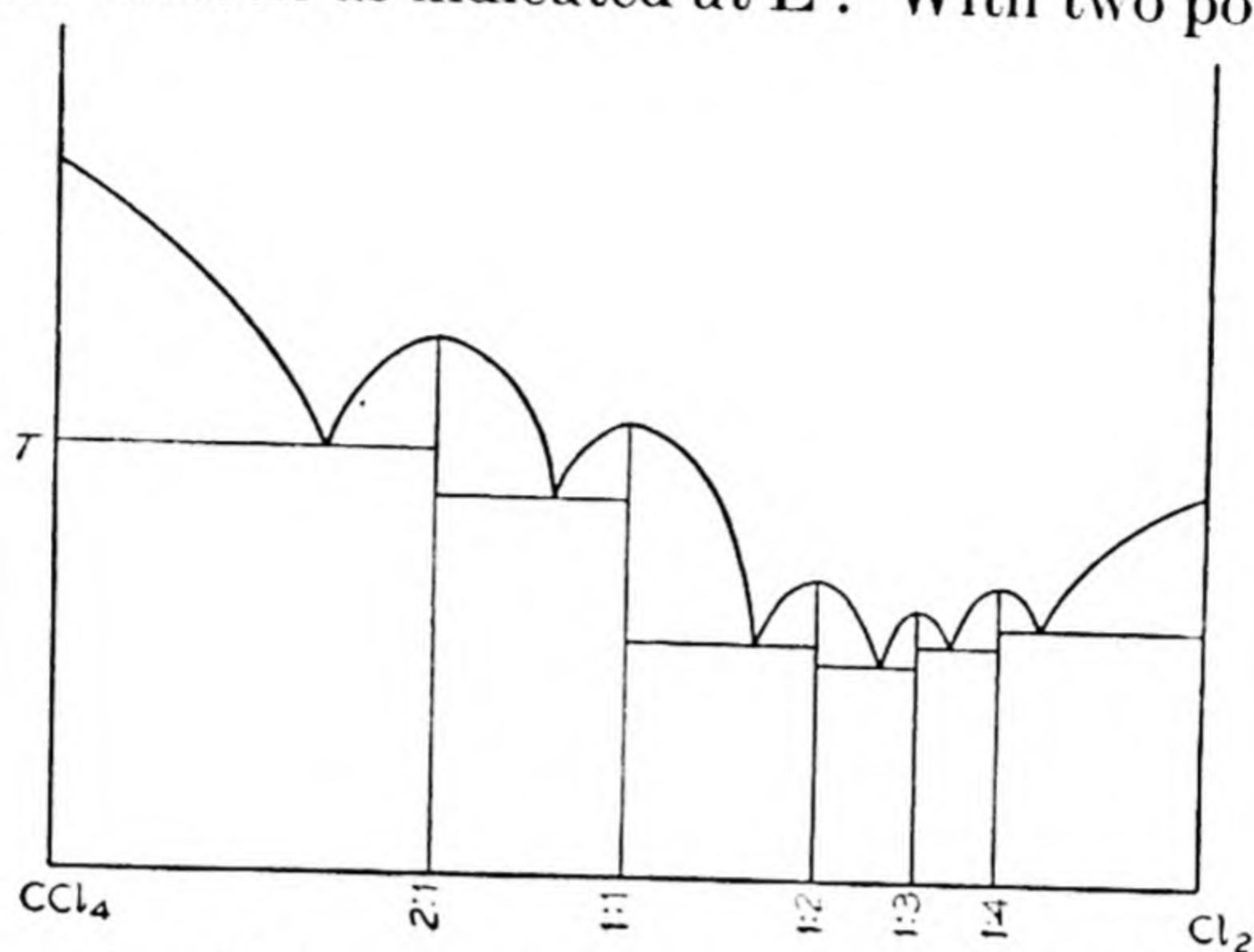


FIG. 7-40. System $\text{CCl}_4\text{-Cl}_2$ (schematic).

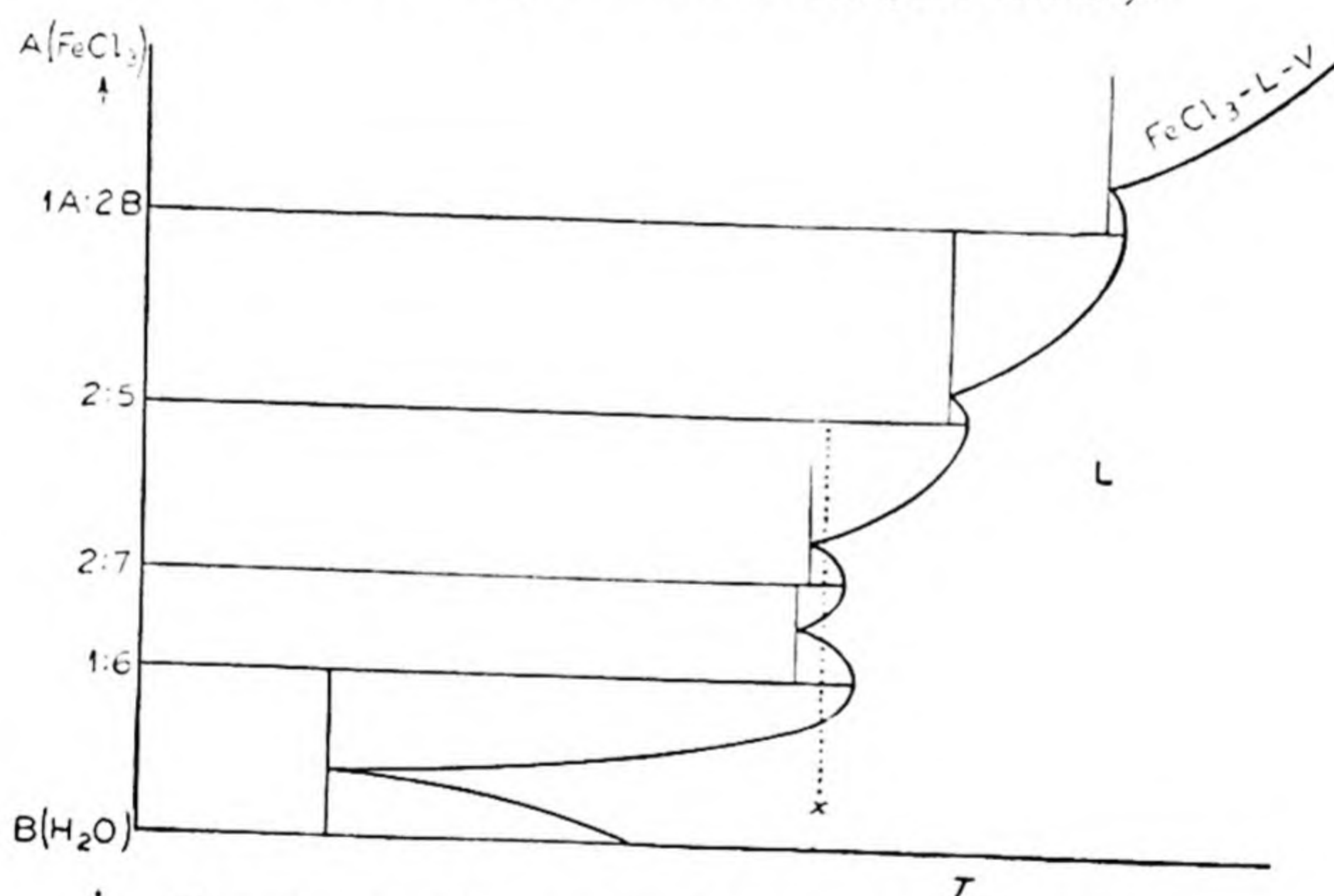


FIG. 7-41. System $\text{FeCl}_3\text{-H}_2\text{O}$ (schematic).

for SO_3 , the lower melting one (α) gives a metastable eutectic, E'' , with the first compound, 2:1. Fig. 7-40 is the similar freezing point diagram of the system $\text{CCl}_4\text{-Cl}_2$, with five congruently melting compounds.²⁹

Fig. 7-41 is the freezing point diagram of the system $\text{FeCl}_3\text{-H}_2\text{O}$, with

²⁸ Fig. 7-39 is schematic, following the sketch in J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, London, 1930, Vol. X, p. 352. O. Hultzman and W. Biltz, *Z. anorg. Chem.*, **218**, 369 (1934), reported, in addition, two incongruently melting hydrates, $\text{SO}_3\cdot 9\text{H}_2\text{O}$ and $\text{SO}_3\cdot 7\text{H}_2\text{O}$. Of these only the second has been found in the most recent study of the system, by C. M. Gable, H. F. Betz and S. H. Maron, *J. Am. Chem. Soc.*, **72**, 1445 (1950); these authors also report the compound $\text{SO}_3\cdot 4\text{H}_2\text{O}$, as incongruently melting. See also E. Moles and C. R. de Robles, *Anales soc. españ. fis. y quim.*, **34**, 331 (1936).

²⁹ J. A. Wheat and A. W. Browne, *J. Am. Chem. Soc.*, **60**, 371 (1938).

four congruently melting hydrates.³⁰ If the solution x is evaporated at constant temperature, a series of so-called retrograde liquefactions may be

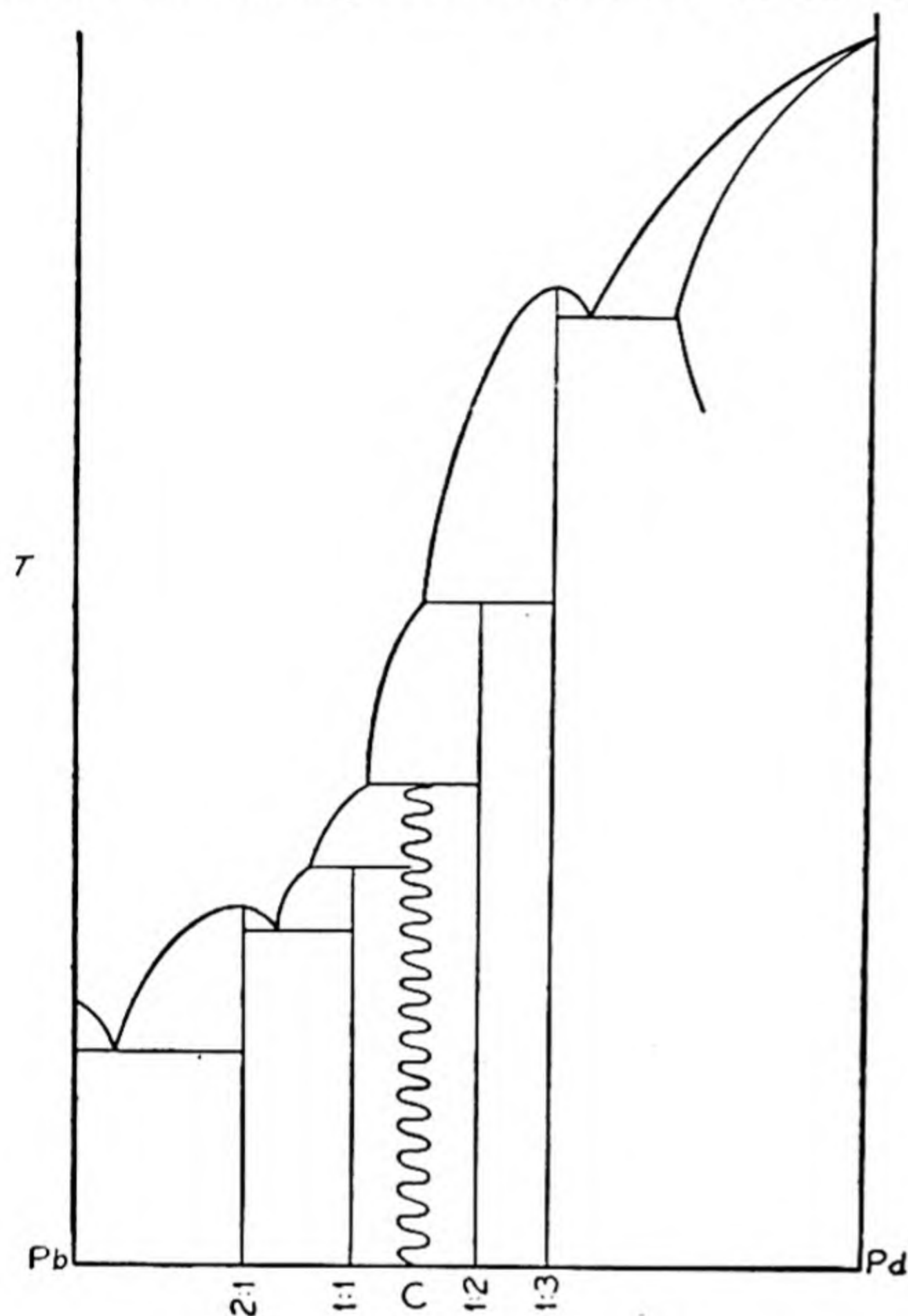


FIG. 7-42. System Pb-Pd.

observed. The solution first becomes saturated with the compound 1:6 and solidifies completely to this compound when the total composition (condensed phases) is 1:6. Further evaporation causes liquid to appear, and the solid redissolves completely but in a more concentrated solution, when the composition reaches the region of unsaturated liquid between the freezing point curves of the first two compounds. What has happened is the decomposition $C \rightarrow L + V$ discussed in connection with the curve E_1M of Fig. 7-34. The process is then repeated, solidifying the second compound (2:7) and decomposing it to a liquid again, between the freezing point curves of this and the next (2:5) hydrate. The 2:5 compound is then obtained as solid on evapo-

rating its solution; but further dehydration now gives the decomposition $C(2:5) \rightarrow C(1:2) + V$, the new solid being the dihydrate.

In Fig. 7-42, the freezing point diagram of the system Pb-Pd shows two congruently and three incongruently melting compounds; the terminal phase at the Pd side, furthermore, is a solid solution, while the other solid phases are assumed to be pure.³¹ The composition of the compound C is in doubt; it may be Pb_3Pd_4 or Pb_2Pd_3 . The schematic figures 7-43(a) and (b) represent a congruently melting compound forming solid solution with both or with only one (A) of the components.³² The system Tl-Bi shows two compounds (possibly non-stoichiometric) of the type of Fig. 7-43(a),³³ while the system Pb-Ca has the compound $PbCa_2$ which forms solid solution with Ca but not with the adjacent compound $PbCa$.³⁴ The maximum

³⁰ H. W. B. Roozeboom, *Z. phys. Chem.*, **10**, 477 (1892).

³¹ R. Ruer, *Z. anorg. Chem.*, **52**, 345 (1907).

³² According to Hansen (*loc. cit.*, p. 978), the compound $PbPd_3$ of Fig. 7-42 forms limited solid solution with Pd but not with $PbPd_2$.

³³ N. Kurnakow, S. Zemczuzny and V. Tararin, *Z. anorg. Chem.*, **83**, 200 (1914); but see also W. Guertler and A. Schulze, *Z. phys. Chem.*, **104**, 269 (1923).

³⁴ N. Baar, *Z. anorg. Chem.*, **70**, 352 (1911).

melting point for these binary phases of variable composition sometimes occurs at a non-stoichiometric proportion of the components, as in the system Tl-Bi just mentioned. For the optical isomers of carvoxime (Fig. 7-1) the supposed "compound" forms continuous solid solution with both components, and in this system the maximum occurs of necessity at the 1:1 ratio. Unsymmetrical cases of continuous solid solution are also known, for two hydrocarbon systems, in which the maxima do not correspond to any simple ratio.³⁵ In these cases it may be better to speak of a "complex," or a binary structure of maximum stability, rather than of a "compound."

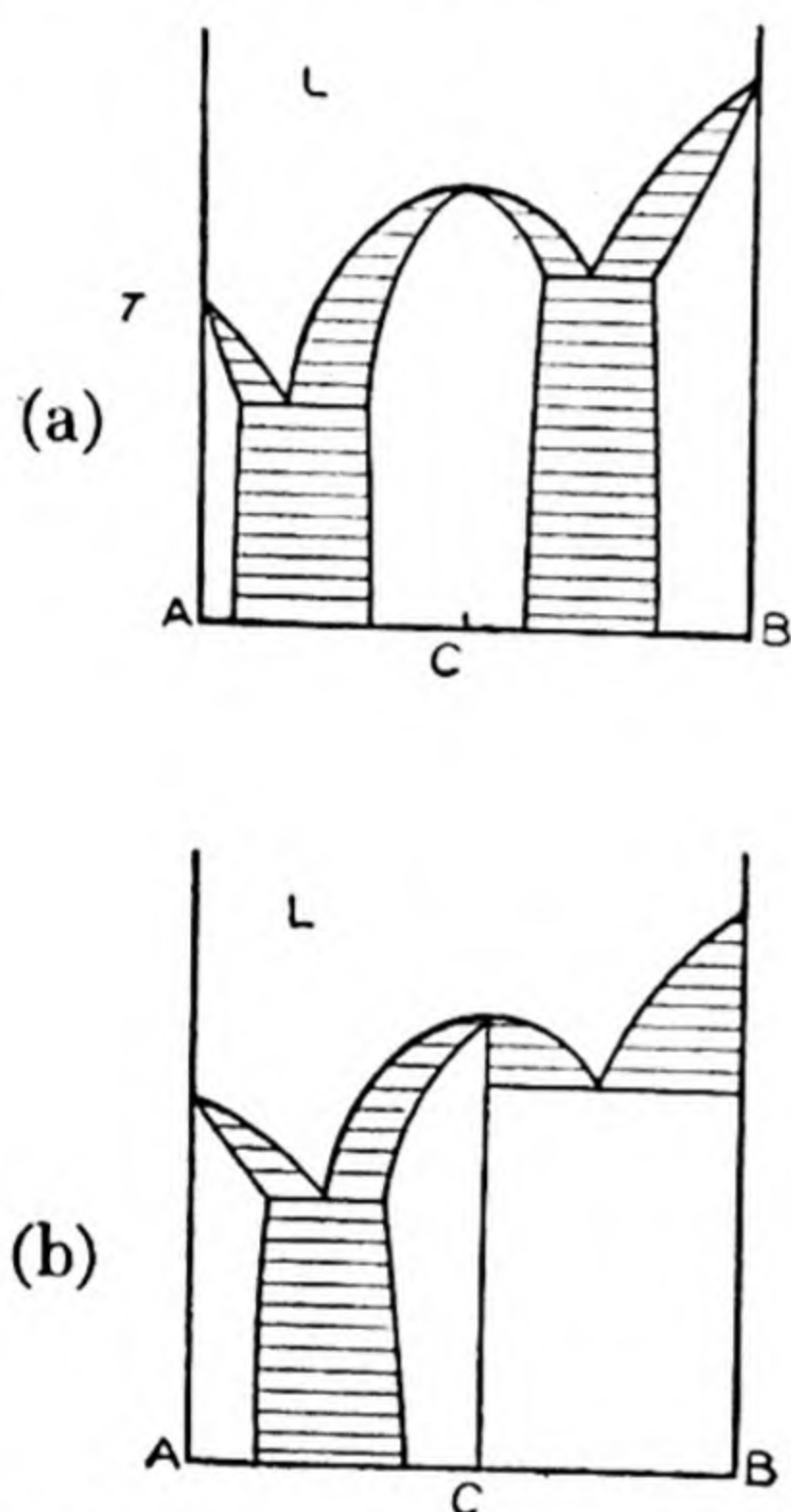


FIG. 7-43. Compound forming solid solution.

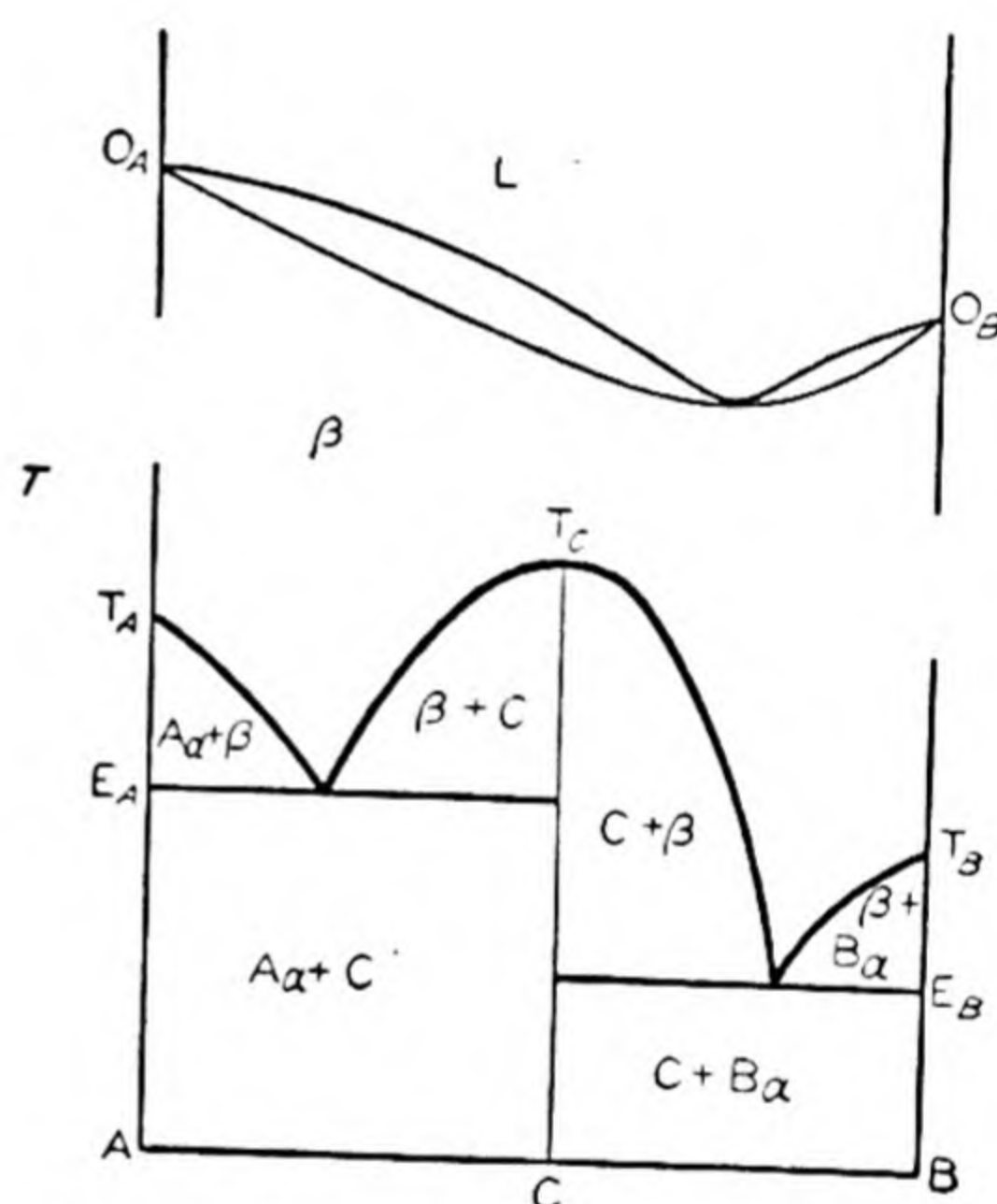


FIG. 7-44. Compound of lower polymorphic forms.

Equilibria similar to those here discussed are also possible for the relations of compounds existing only below the melting point of a system involving continuous solid solution at the temperature of the melting point diagram. In Fig. 6-4(c) the solid solution is shown reaching down (in the condensed diagram) to a eutectoid involving the two lower polymorphic forms of the components, these being immiscible. If these forms should react to form a compound reaching a congruent transition point in respect to the solid solution β of the higher forms, the condensed diagram may appear, schematically, as in Fig. 7-44. Here O_A and T_A are respectively the melting and transition points of the component A; T_c is the congruent transition point of the compound. Instead of the single eutectoid of Fig. 6-4(c), there are

³⁵ H. L. Fink, M. R. Cines, F. E. Frey and J. G. Aston, *J. Am. Chem. Soc.*, **69**, 1501 (1947).

now two — E_A for the equilibrium $A_\alpha\beta C$ and E_B for the phases $C\beta B_\alpha$. The curve through T_c , enclosing heterogeneous areas of $\beta + C$ and $C + \beta$, is to be distinguished, of course, from a miscibility gap involving conjugate solid solutions. The whole figure is identical, in fact, with Fig. 7-3, except for the states involved. In Fig. 6-5(e) the maximum m of the $\alpha \rightleftharpoons \beta$ transition occurs near the composition FeNi_2 , indicating some compound formation between the lower forms.

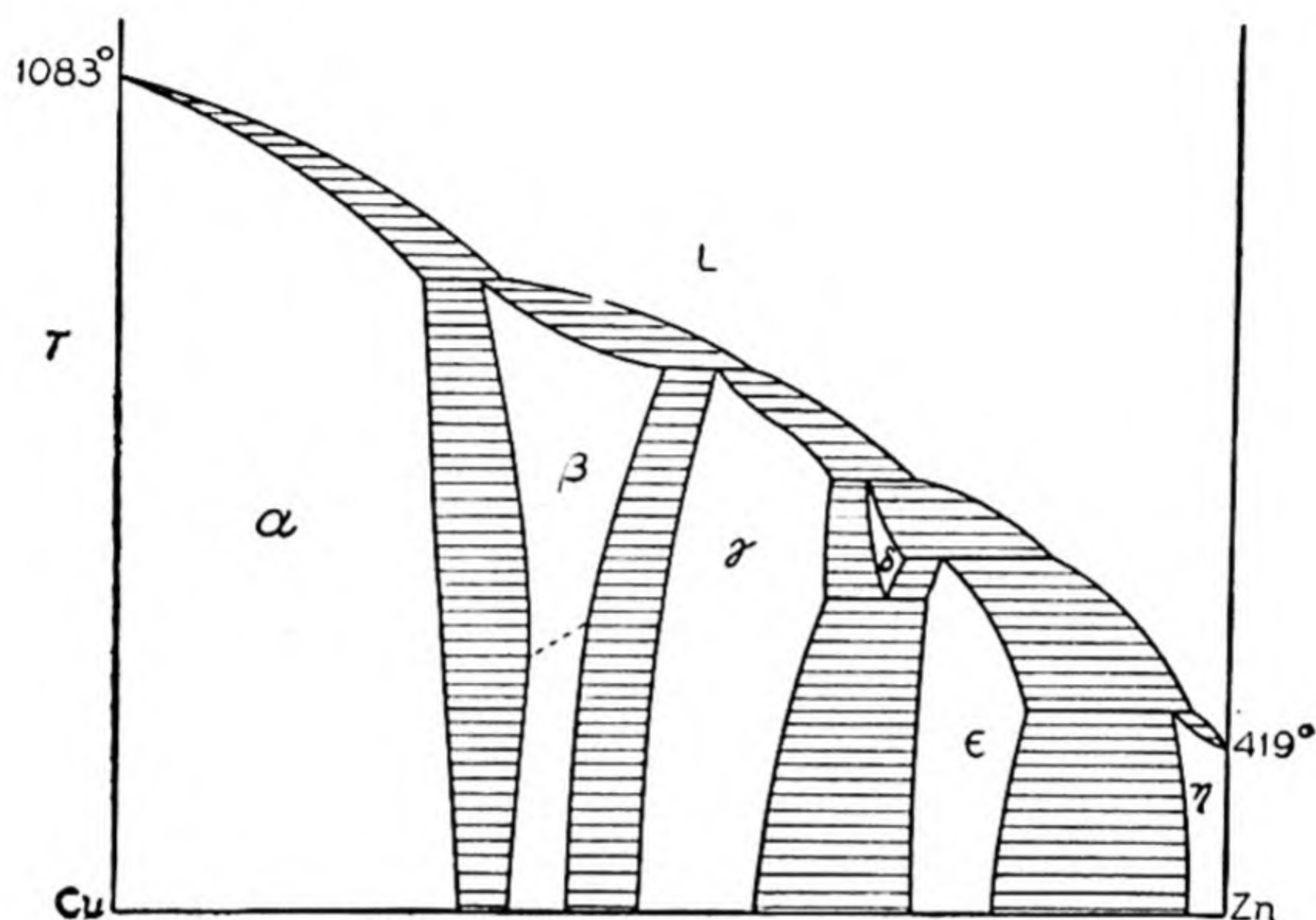


FIG. 7-45. System copper-zinc (schematic).

Fig. 7-45 is the phase diagram of the Cu-Zn system, shown schematically to bring out the relations.³⁶ There is a series of solid phases of variable composition, the α phase being a substitutional solid solution of Zn in the face-centered cubic structure of Cu, the η phase a similar solid solution of Cu in the hexagonal structure of Zn. These are known as the primary phases or primary solid solutions of the system. The four intermediate (secondary) phases have intermediate and more complex structures, and whether or not they are related to definite compounds cannot be inferred simply from the phase diagram. Nevertheless they may in a sense be considered as based on intermetallic compounds dissolving adjacent phases to some extent, and hence of variable composition. The phases β , γ , ϵ include, successively, the atomic ratios 1:1, 5:8, 1:3, which are those expected according to the Hume-Rothery "electron concentration rules" for intermetallic phases;³⁷ but the δ phase, with the most complex structure and with a completely circumscribed region of existence, seems to be special and unusual. These intermetallic phases may be regarded as a series of non-stoichiometric, incongruently melting compounds, since the freezing

³⁶ R. Ruer and K. Kremers, *Z. anorg. Chem.*, **184**, 193 (1929).

³⁷ W. Hume-Rothery, *loc. cit.*, p. 112; also *J. Inst. Metals*, **35**, 309 (1926).

point curve shows a series of peritectic breaks but no maximum. The dotted line across the area of the β phase indicates a second-order transition between the "ordered" and "disordered" structure of the phase; it is not a phase boundary.

This diagram bears a certain similarity to that of the system sodium myristate-water (Fig. 7-46, schematic), and other homologous soap-water systems, in which variable binary phases with limited regions of existence are found, but which are of a mesomorphic (liquid crystalline) nature.³⁸ The soap itself is polymorphic, existing in a number of liquid crystalline forms, as mentioned in Chapter II, so that there is a series of transition points for pure soap, below the final melting point O_A , to isotropic liquid. Each of these phases, moreover, appears to be of variable composition, holding water in "solid solution," the expression being used to distinguish as "solids" all anisotropic phases. All the transition points are lowered by the water, giving a series of transition curves of the type of Fig. 6-7(a). Even the lowest temperature form, known as "curd fibers," apparently contains water. The solubility curve of the soap, running from the eutectic E to the melting point O_A , is interrupted by two variable binary phases, S_1 and S_2 , each of which reaches a maximum melting or transition point (m_1 and m_2) at which the mesomorphic phase has the same composition as the isotropic liquid. There are consequently three eutectic points (E , E_1 , E_2) in the system. The field of each of these binary phases is furthermore terminated with decreasing T at a eutectoid type of invariant point (a 3-phase tie-line of the condensed system), E'_1 and E'_2 . The maxima seem to have no stoichiometric significance, and whether or not the compositions of the maxima are independent of P and T is not known. The phase S_1 is known as middle soap, and S_2 as neat soap, with some indication

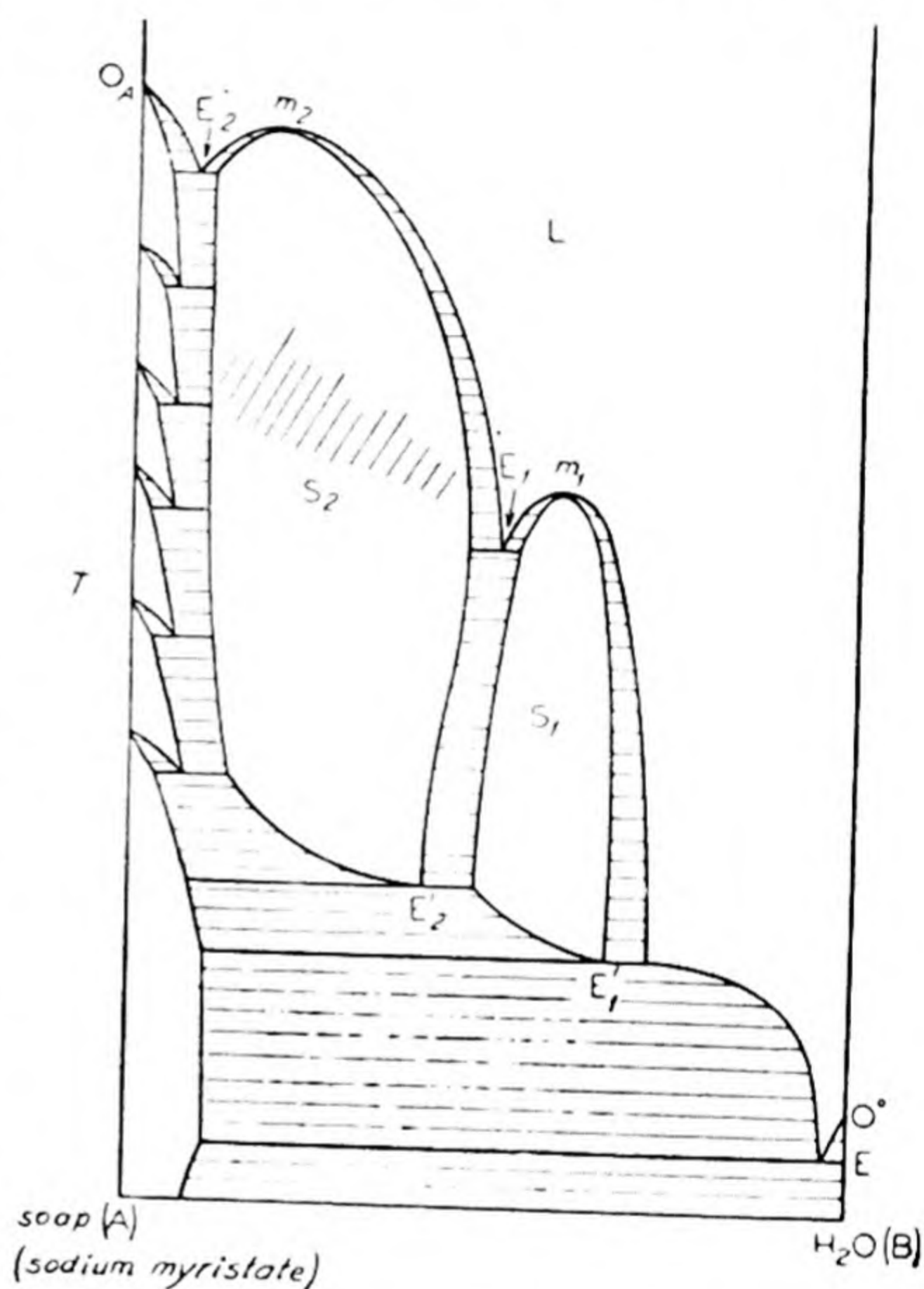


FIG. 46. System soap-water (schematic).

³⁸ R. D. Vold, R. Reivere and J. W. McBain, *J. Am. Chem. Soc.*, **63**, 1293 (1941)

of a difference, as shown by the shaded area, in properties between the higher and lower temperature portions, the higher portion being called "superneat" soap, the lower "soap boiler's neat soap." Finally the section of the solubility curve rising from the eutectic E shows the phenomenon of the Krafft point, mentioned in Chapter V, characteristic of solutions of colloidal electrolytes.

F. Compound Having Both a Congruent Melting Point and a Congruent Sublimation Point

If the congruent sublimation or vaporization curve $C = V$, rising in P and T , meets the V surface of the L/V loop, forming a singular point S involving three phases, LCV , with C and V having the same composition, then S may be called the congruent sublimation point of the compound. Up to this point the compound is said to "sublime without decomposition," but it must be remembered that, both here and in the process of congruent melting "without decomposition," it is not implied that the compound does not dissociate into its components in the V or L phase, but only that the analytical compositions of the two phases, C and V or C and L , are the same. Above the point S (as below the point M of Fig. 7-34) the compound no longer undergoes this congruent transition but decomposes heterogeneously into $L + V$. The equilibrium $C \rightleftharpoons L + V$ or the curve LCV , which originates at the point S , is the same as that originating at point M of Fig. 7-34, so that the relations in the present case are only a modification of those of that figure. Point S , like point M , is a singular point of type m , being the intersection of the congruent vaporization curve with the 3-phase intersection curve already discussed in connection with Fig. 7-34.

An example is the system $\text{NH}_3(\text{A})\text{--H}_2\text{S}(\text{B})$, forming the solid compound $2\text{NH}_3\cdot\text{H}_2\text{S}$, shown schematically in Fig. 7-47.³⁹ Now the C plane is bounded by the two congruent transition curves interrupted by the decomposition curve $C \rightleftharpoons L + V$ between S and M . In this case the L/V loop is not of the simple, ascendant type from A to B but is azeotropic with a minimum in P/c . The point N , on that portion of the intersection curve (continuous from E_1 to E_2) which represents the solubility of C in A -rich liquid at the pressure of the system, is the intersection with the pressure minimum (and hence temperature maximum) of the L/V loop. At N , therefore, with V and L having the same composition, the order of the three phases of the intersection curve changes from VLC to LVC ; at S , where $C = V$, the order becomes LCV ; and at M , where $C = L$, it becomes CLV , so to continue to E_2 , except for interruption between K_1 and K_2 , by the

³⁹ F. E. C. Scheffer, *Z. phys. Chem.*, **71**, 214, 671 (1910); **76**, 161 (1911).

critical curve. The "intersection curve" has therefore crossed, successively, the pressure minimum of the L/V loop (azeotropic curve), the congruent sublimation curve, and the congruent melting curve. The points K_1 and K_2 are the critical end-points at which the critical curve, shown as a dashed curve from K_A to K_B , is interrupted by the solubility curve E_2M of C in B-rich liquid (see Chapter V, Fig. 5-16).

At the point S the compound has changed, with rising T , from congruently to incongruently subliming. The transformations involved are shown in the isothermal sections of Fig. 7-48. Fig. 7-48(e), but without

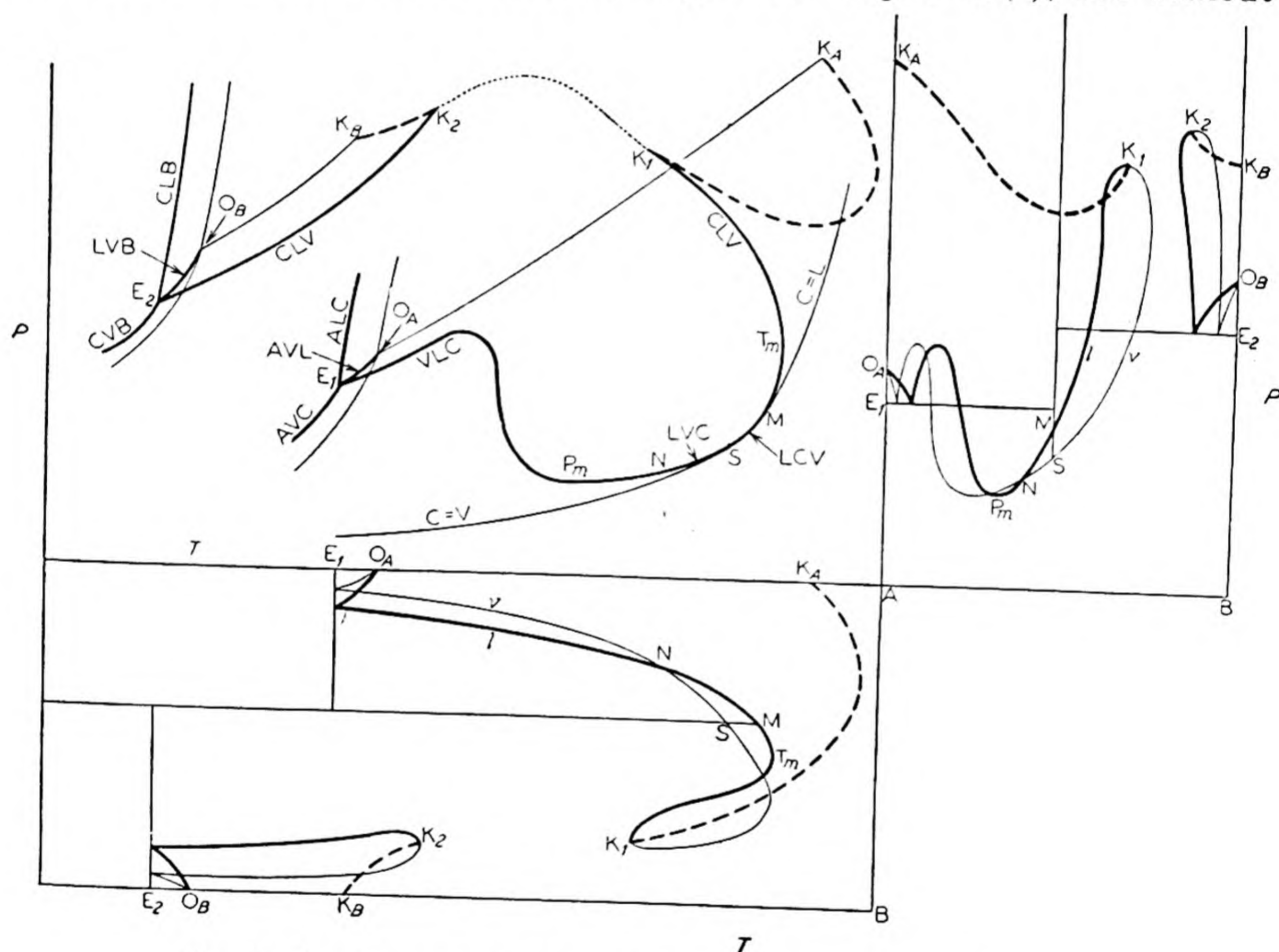


FIG. 7-47. Compound with congruent sublimation point.

the minimum in the L/V loop, or as in Fig. 7-49, is a type observed in the system aniline (A)– SO_2 (B) studied in the temperature range 5° – 50° ; a 1:1 compound is formed, vaporizing incongruently as here shown, the components being both liquids at the P and T studied.⁴⁰

G. Polymorphism of Compound

If a binary compound, e.g. $\text{CaO} \cdot \text{CO}_2$ or calcium carbonate, exists in two polymorphic forms, C_α at lower, C_β at higher T , the composition plane of

⁴⁰ A. E. Hill, *J. Am. Chem. Soc.*, **53**, 2598 (1931).

the compound will be divided in two parts by a P/T transition curve, with positive or negative slope. This $C_\alpha C_\beta$ transition curve will meet one of the boundaries of the plane and cause a break in that univariant curve, or any

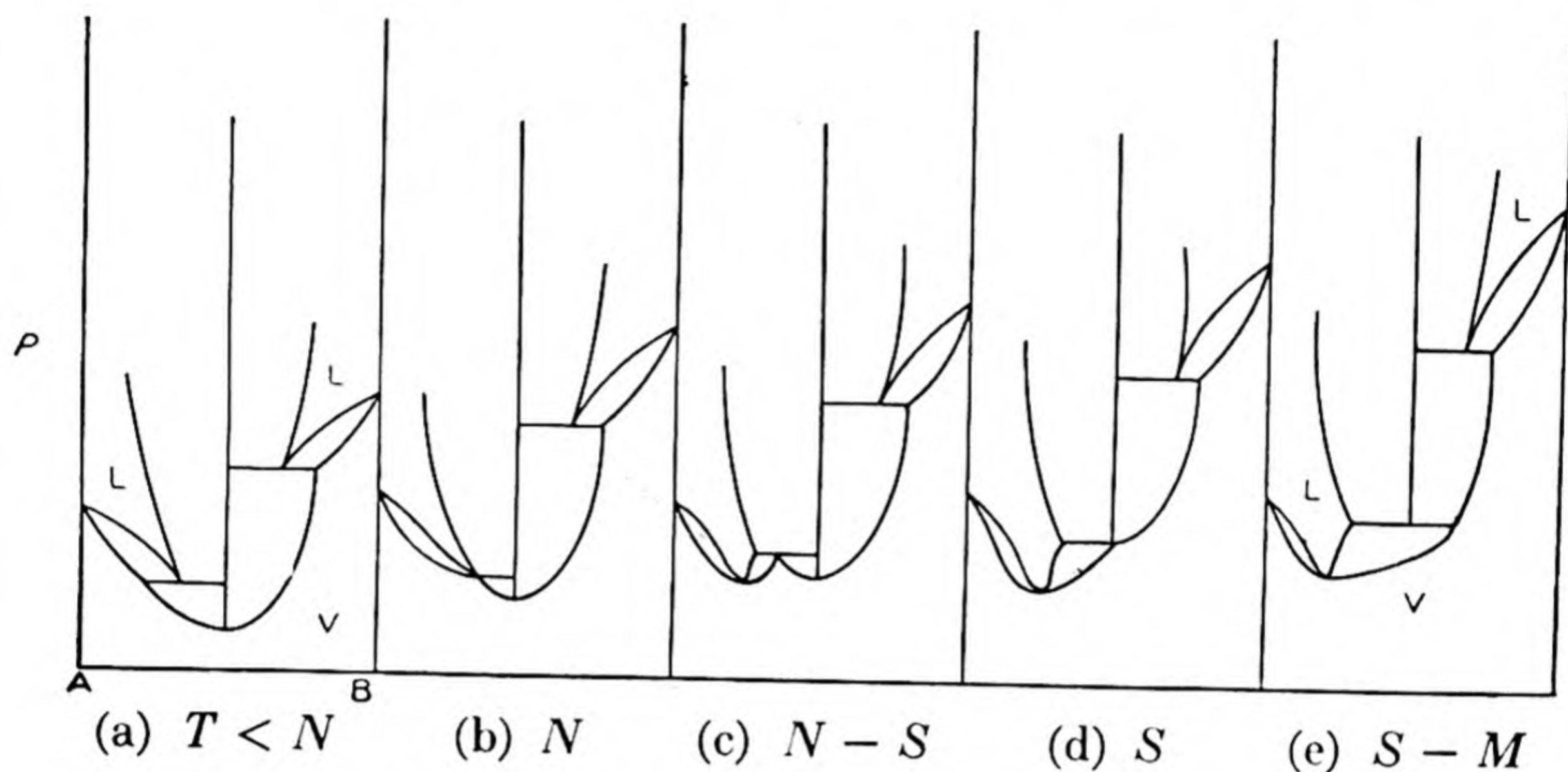


FIG. 7-48. Isotherms of Fig. 7-47; for $K_B > M$ in temperature.

of its projections. The boundaries involved may be, of course, the congruent transition curves or any of the decomposition curves already discussed, $C \rightleftharpoons A + B$, $C \rightleftharpoons A + V$, $C \rightleftharpoons A + L$, $C \rightleftharpoons L + V$ (and even $C \rightleftharpoons L_1 + L_2$).

If the "break" occurs on a congruent transition curve ($C = V$ or $C = L$), it will involve only three phases, C_α , C_β , L , for example. But it will be a real invariant point nevertheless, for with all three phases having the same composition we are dealing with what is effectively a unary system at a triple point. As stated in Chapter I, the order of the system (number of components) must be determined with reference to the phenomenon under consideration.

If the break occurs on a decomposition curve (such as ACV or ACL), it will be a binary quadruple, invariant transition point. If the vapor phase is involved, then the phase C_α will be the stable form and C_β the metastable form at the pressure of the system, at temperatures below that of the point Q_v , which involves the four phases A , C_α , C_β , V ; and at the same temperature the metastable form will have a higher decomposition P than the stable form. If the point Q_v does not occur too far below the eutectic of the system, the compound transition curve $C_\alpha C_\beta$ may cross, in P/T projection, the solubility curve of the compound and thus give rise to a second quadruple point, Q_l , involving the phases C_α , C_β , L , V . Below the temperature of Q_l the metastable form C_β will have a higher solubility than the stable form. The relations are shown in Fig. 7-50; the phases involved in each

invariant are shown by circles in the T/c projection, and two circles for the composition C indicate that the two forms of the compound are involved.

The point Q_1 has already been discussed (Fig. 7-14). For Q_v and Q_l , it must be noted that any univariant 3-phase equilibrium involving both C_α and C_β or the polymorphic transition of C must be coincident in P/T projection, with this (unary) transition curve of the (pure) solid compound. Since the slope of this curve may be positive or negative, Q_v will be below

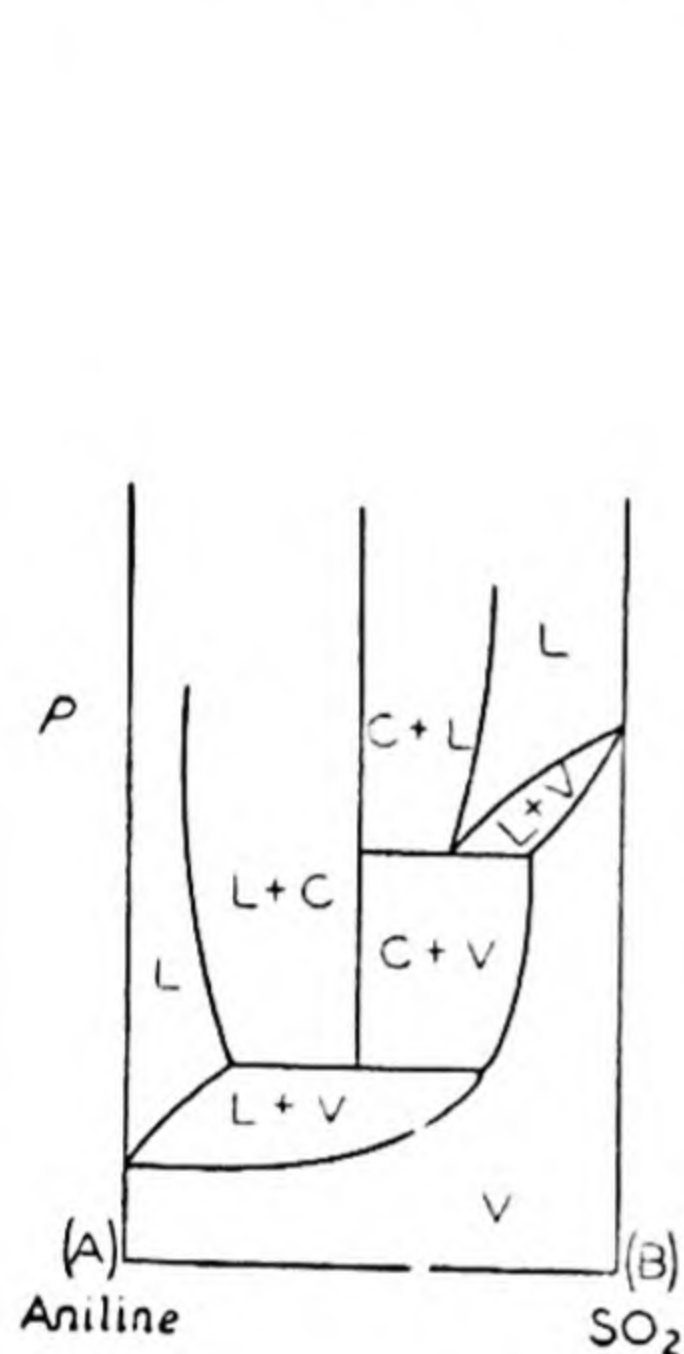


FIG. 7-49. A schematic isotherm of the system aniline-sulfur dioxide.

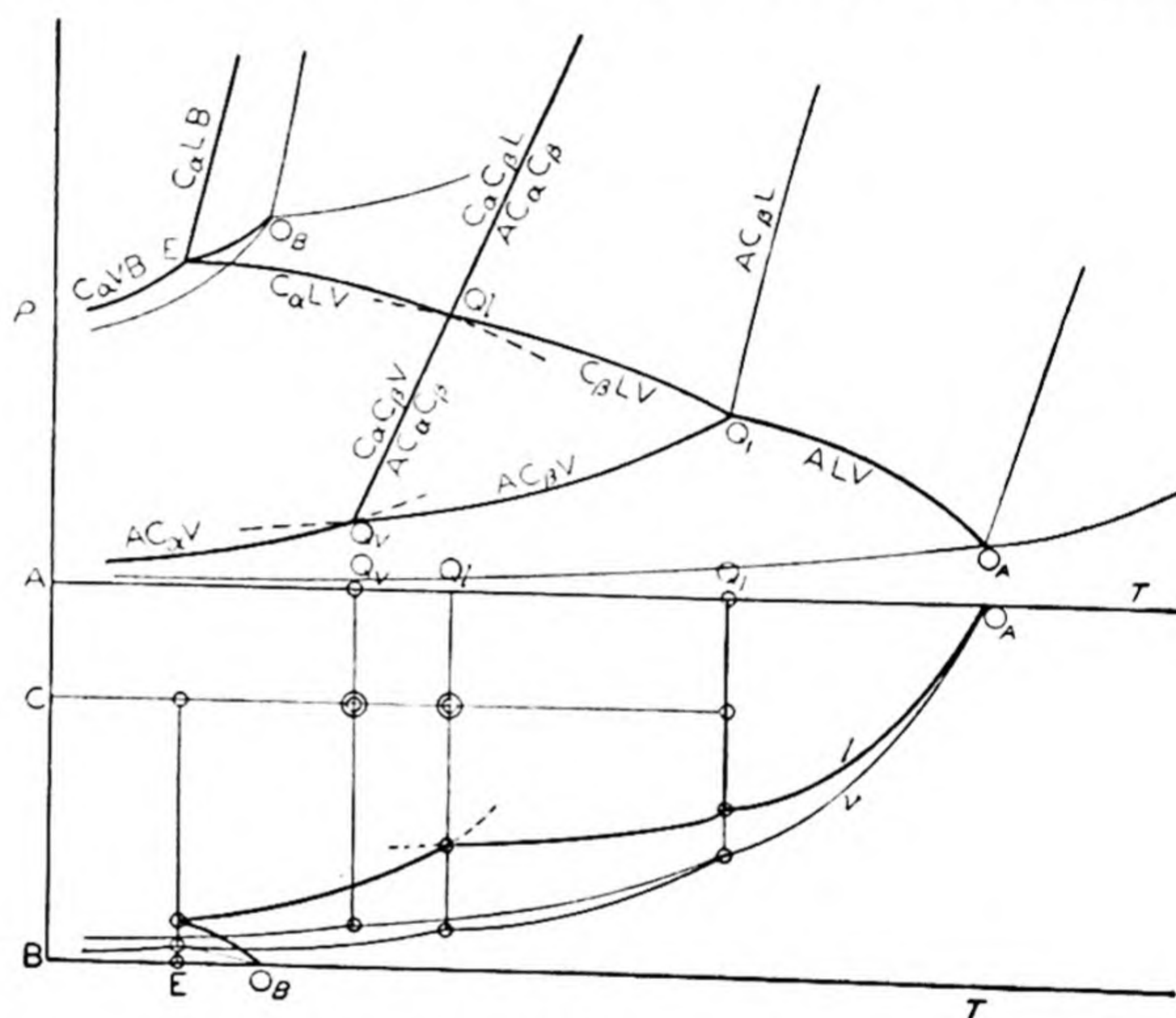


FIG. 7-50. Polymorphism of compound.

Q_l in P but may be higher or lower in T . The relations in Fig. 7-50 have been exaggerated for clarity, but ordinarily the line $Q_v Q_l$ will be so short that, whatever the slope, the two temperatures will be practically identical. Q_l , involving a liquid solubility, may be determined, of course, as the intersection of the solubility curves of the two forms, from the measurement either of the concentration of L or of the vapor pressure of the saturated solutions. Q_v could be determined as the intersection of the vapor pressure curves of the decompositions $AC_\alpha V$ and $AC_\beta V$, but its temperature will usually be indistinguishable from Q_l . Schematic sections are shown in Fig. 7-51 (isotherms) and Fig. 7-52 (isobars) for the relations under discussion. The invariant Q_l involves the *unary* polymorphic transformation of the compound; hence, according to the principle given for such *lower order* equilibria in Chapter I, section H-3, the quantity of the liquid phase during the invariant reaction will be constant. Point Q_l is, in other words, entirely similar to point Q of Fig. 6-7(c).

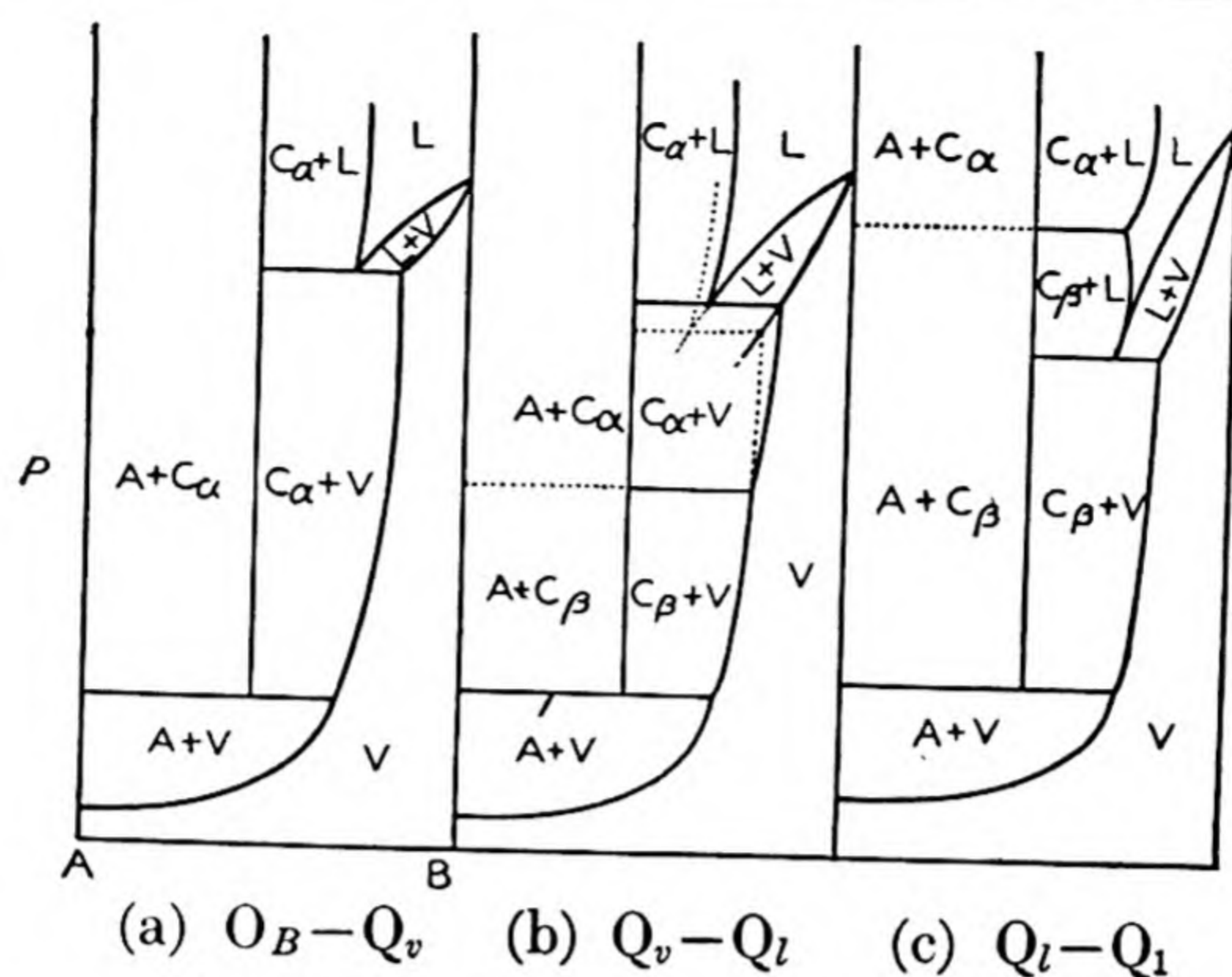


FIG. 7-51. Isotherms of Fig. 7-50.

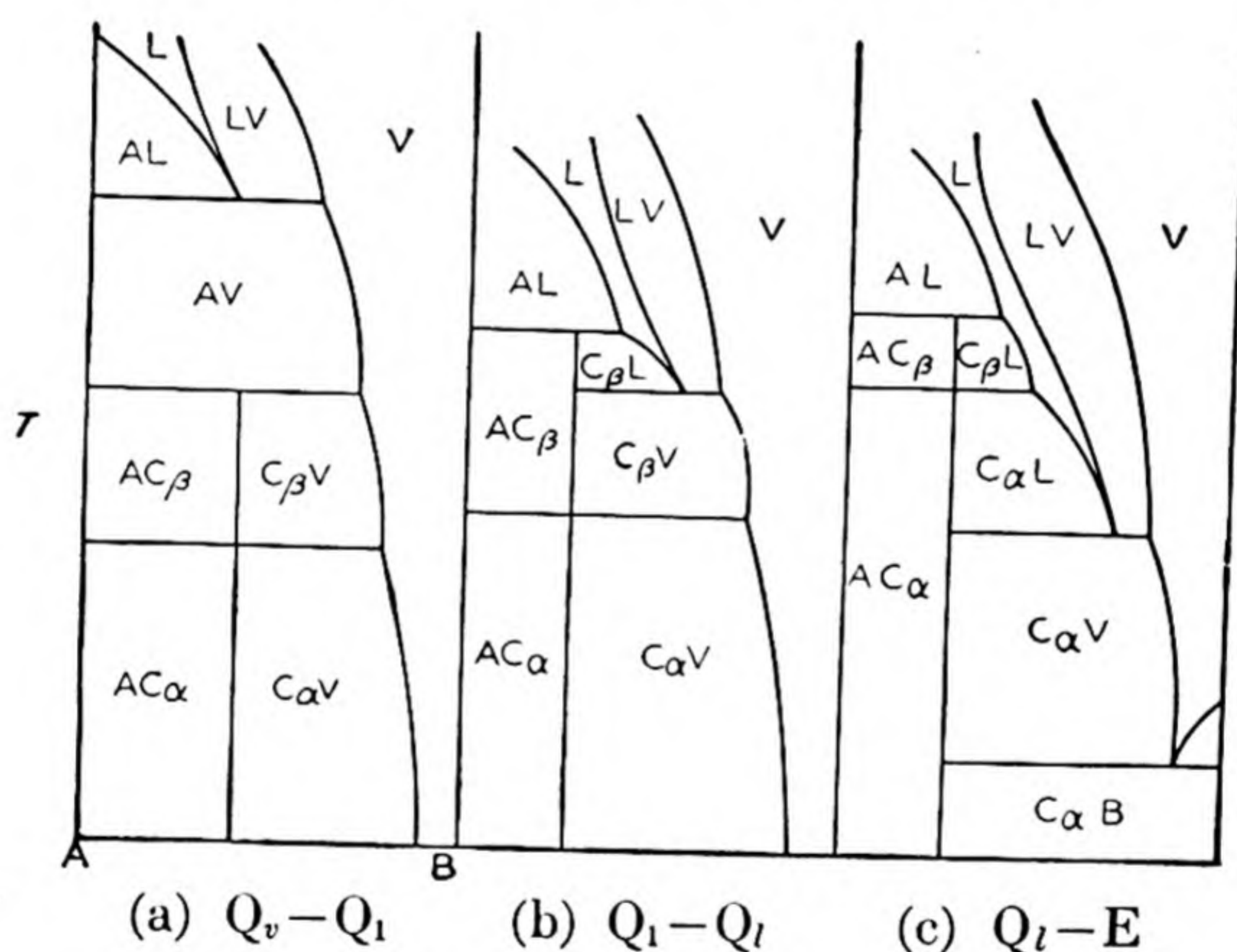


FIG. 7-52. Isobars of Fig. 7-50.

These relations are illustrated by the two examples of Figs. 7-53 and 7-54. Fig. 7-53 is the condensed diagram of the system $\text{Ag}_2\text{SO}_4\text{-H}_2\text{SO}_4$,⁴¹ involving the two binary compounds $C (= \text{Ag}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$ the "bisulfate") and $D (= \text{Ag}_2\text{SO}_4 \cdot 2\text{H}_2\text{SO}_4)$, both incongruently melting. The bisulfate exists in two forms, C_α stable below Q_l , 66° , C_β above this transition temperature. Q_l of Fig. 7-53 therefore corresponds to Q_l of Fig. 7-50. Q_1 is the incongruent melting point (122.5°) of the β -bisulfate, and Q_2 (36°) is the incongruent melting point of the compound D , or the temperature of the condensed invariant reaction $D + \text{cals.} \rightleftharpoons C_\alpha + L$. Q_2' (39°) is the corresponding metastable invariant in which the higher form, C_β , is involved in place of C_α .

⁴¹ J. Kendall and A. W. Davidson, *J. Am. Chem. Soc.*, **43**, 979 (1921).

In the system $\text{CaCl}_2\text{-H}_2\text{O}$, the classical investigation by Roozeboom showed two forms of the tetrahydrate, α and β , the β form being metastable throughout at the pressure of the system. Fig. 7-54 represents

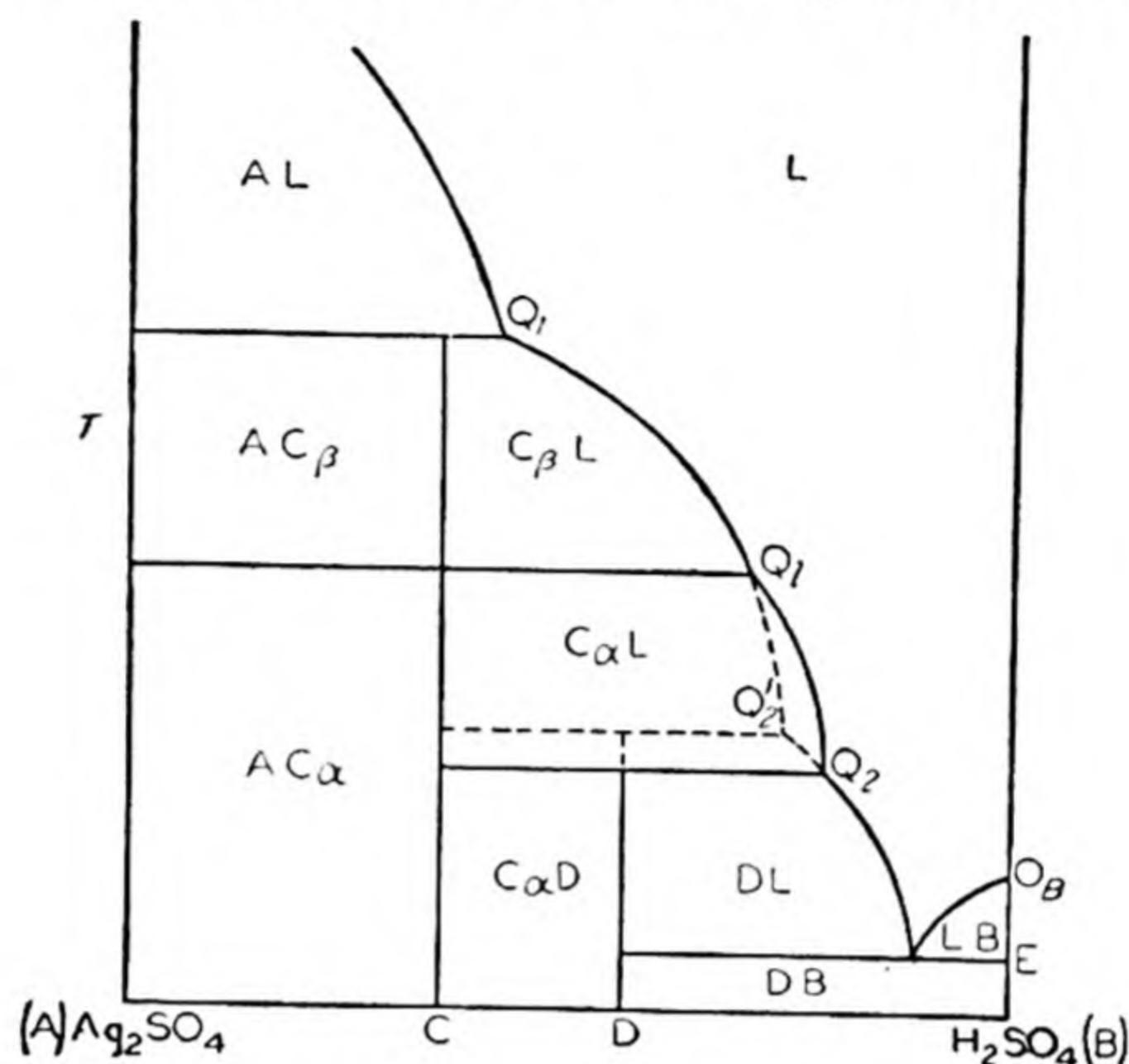


FIG. 7-53. System $\text{Ag}_2\text{SO}_4\text{-H}_2\text{SO}_4$ (schematic).

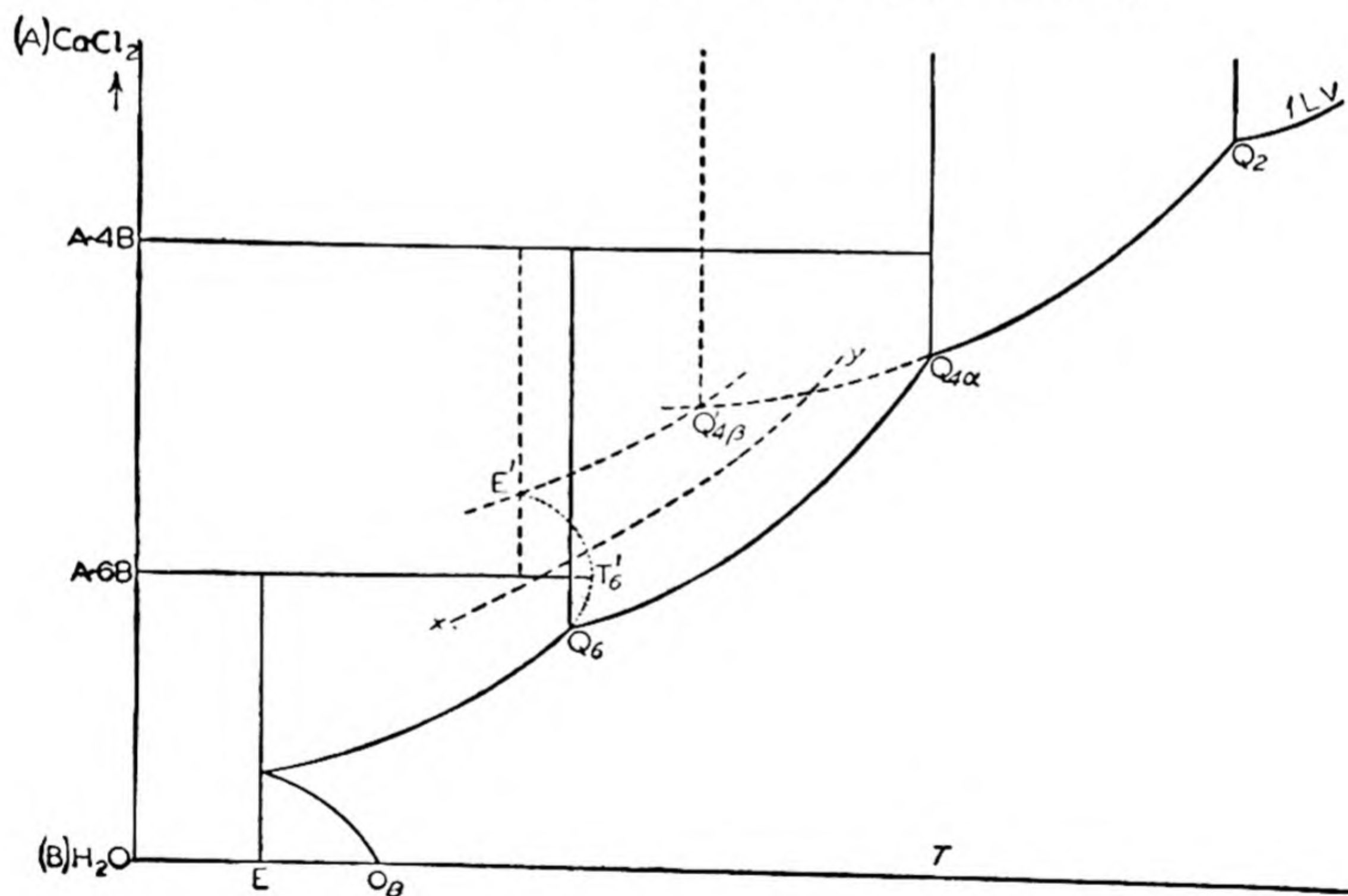


FIG. 7-54. System $\text{CaCl}_2\text{-H}_2\text{O}$ (schematic).

the (condensed) freezing point relations (schematic).⁴² The hydrates are 1, 2, 4 α , 4 β , 6; Q₆, Q_{4 α} , and Q₂ are transition points, although both the hexa- and the dihydrates almost reach congruent melting points. T'₆ is the metastable congruent melting point of the hexahydrate. The metastable solubility curve of $\beta\text{-CaCl}_2\cdot 4\text{H}_2\text{O}$ intersects the metastable decomposition

⁴² B. Roozeboom, *Rec. Trav. Chim. Pays-Bas*, 8, 1 (1889).

curve, L6V, of the hexahydrate at the metastable incongruent eutectic E' ; and with rising T it intersects the metastable extension of the solubility curve of the dihydrate at the metastable transition point $Q'_{4\beta}$. The curve xy in Fig. 7-54 shows the relative position of the solubility curve of still a third form of the tetrahydrate, $\gamma\text{-CaCl}_2\cdot 4\text{H}_2\text{O}$, also metastable, reported by Bassett.⁴³ The vapor pressure curves (measured and discussed by

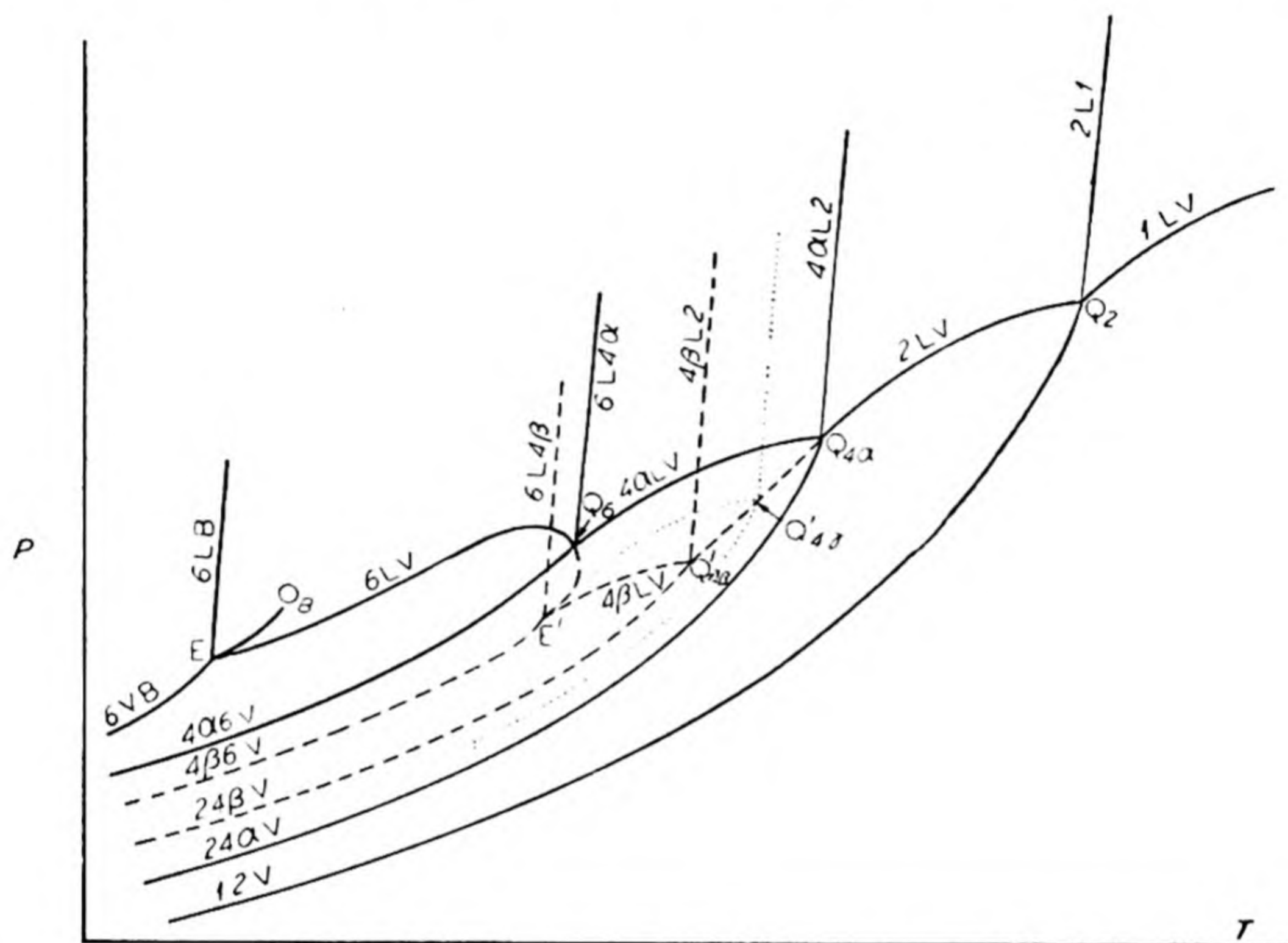


FIG. 7-55. Vapor pressure curves of system $\text{CaCl}_2\text{-H}_2\text{O}$ (Roozeboom).

Roozeboom) are shown in Fig. 7-55, adapted, schematically, from Roozeboom's original figure. The light dotted curves, meeting at $Q'_{4\gamma}$, have been inserted upon Roozeboom's diagram, to represent the probable relations for the hydrate $\gamma\text{-CaCl}_2\cdot 4\text{H}_2\text{O}$.

H. Optical Isomers

Binary systems of optical isomers may form compounds (racemates) and will therefore be discussed at this point.

1. A chemical compound X containing in its molecular structure a single element of optical asymmetry, such as an open chain carbon compound with a single asymmetrical carbon atom, constitutes a pseudobinary system, in which the two forms ($d\text{-X}$ = component A, $l\text{-X}$ = component B) are thermodynamically identical and equally stable. The solid forms, which we shall here write X_d and X_l respectively, may crystallize separately as pure

⁴³ H. Bassett, G. W. Barton, A. R. Foster and C. R. J. Pateman, *J. Chem. Soc.*, 1933, p. 151.

solid phases in the presence of each other, or form solid solutions, limited or unlimited. They may also form a compound which, if it appears at all on the melting point curve of the system, must have a congruent melting point since the system must always be symmetrical. In the absence of compound formation, the binary diagram will be either a continuous solid solution curve with or without a central minimum or maximum, or a simple eutectic diagram involving the pure solid forms or conjugate solid solutions.

In any case the phase diagram is symmetrical, the two optical isomers having identical melting points and vapor pressures, and the maximum or the minimum, whatever the nature of the solid or solids, being always at the 1:1 composition. As a result all the phase transitions of a racemic or inactive sample are congruent, the isolated sample suffers no fractionation (resolution) during phase transition, and its phase behavior is completely *unary*. This is so even when the sample is treated with an "inactive" additional substance, when it continues to act as a single component. Unary behavior in the Phase Rule sense is, therefore, strictly not proof that an inactive sample is not a 1:1 mixture of substances which are thermodynamically equivalent isomers. The binary nature of such materials, if it cannot be brought out by visual examination or mechanical separation, can be made evident only when they are subjected to the action of an asymmetric medium. If treated with an already resolved or active sample of any substance — not necessarily an isolated isomer of the original material itself — its binary nature becomes evident in that the two isomers then behave differently in phase reactions.

The internal or homogeneous equilibrium "curve" of such a substance as a pseudobinary system, in the L or V phases (cf. Chapter VI-F), will be the 1:1 ratio of the two forms at any P and T , since this ratio will represent the maximum entropy. If this equilibrium distribution is reached, the substance is said to be racemized (r -X or X_r). Racemization will be assumed to occur only in the phases L and V. If this racemization is instantaneous, the substance behaves as a one-component system, and its constants (T and P of triple point, for example) will be those of the 1:1 ratio or the central point of the binary diagram. Since this may be a eutectic mixture, a solid solution, or a compound, in each case acting as a single component, the constants may be higher or lower than those of the separate isomers. If the racemization is completely hindered, the two forms constitute a true binary system; and if the racemization proceeds at a finite rate, the substance is a pseudobinary system. In such "binary" systems the analytical difference from phase to phase or the analytical variation in a variable phase is, of course, the optical rotation.

Of the possibilities here listed for the melting point relations of optical

isomers, no case seems to be known of continuous solid solution with minimum melting point. On theoretical grounds Van Laar⁴⁴ proposed, in fact, that the only possibilities should be: (1) solid solution with constant melting point, as in a few known cases including camphoroxime;¹ (2) solid solution with maximum melting point, as in carvoxime¹ and in monobornyl malonate,⁴⁵ attributable to a racemic compound forming continuous solid solution with each isomer; and (3) a racemic compound forming eutectic mixtures with the isomers, as in mandelic acid.¹ The theoretical necessity for such limitation, however, seems doubtful. On the experimental side, moreover, we note that although the simple eutectic behavior of the system *d*- and *l*-pinene⁴⁶ has been suspected⁴⁷ of being the result of impurities, further examples have recently been reported, such as *d*- and *l*- β -benzoylhydratropic acid.⁴⁸

If the plane of a racemic compound *C*, in the $P/T/c$ space model, meets, as in Fig. 7-9, a decomposition curve of the type ACB (here X_dCX_l , or $C + \text{cals.} \rightleftharpoons X_d + X_l$) with rising temperature, we have the P/T projection of Fig. 7-56 and the isotherms of Fig. 7-57; if the compound decomposes with decreasing temperature we would have the analog of Fig. 7-13. Since the system is symmetrical, the compound must at all times vaporize (as it must also melt) congruently, up to its decomposition at *Q*. The curves X_dVC and CVX_l appear superimposed, as do also the curves X_dV and VX_l , in the P/T projection, again because of the symmetry. The point *Q* is, therefore, the intersection of four 3-phase equilibria, as usual. In addition, however, the congruent vaporization curve $C = V$ also ends at *Q*. Hence *Q* may be fixed as the intersection of the two vapor pressure curves for the phases $C + V$ and $X_d + V + X_l$, as was pointed out by Meyerhoffer.⁴⁹ It must be noted that the variance at *Q* is zero because the equilibrium involves the four phases X_d , X_l , *C*, *V*. The fact that *C* and *V* have the same composition does not here constitute a thermodynamic restriction, for this circumstance, as pointed out under Fig. 7-1, is simply part of the general requirement of symmetry for the system.

2. A system consisting of one form of such a substance and a symmetrically constituted substance, *Y*, is binary, and the phase diagram is identical for the binary system of *Y* with either form of *X*. The solubility of X_d in a substance such as water (*Y*), in other words, is identical with that of X_l in

⁴⁴ J. J. Van Laar, *Z. phys. Chem.*, **64**, 257 (1908).

⁴⁵ E. B. Abbot, E. W. Christie and A. McKenzie, *Berichte*, **B-71**, 16 (1938).

⁴⁶ J. D. M. Ross and I. C. Somerville, *J. Chem. Soc.*, 1926, p. 2770.

⁴⁷ J. Timmermans, *Bull. Soc. Chim. Belg.*, **39**, 243 (1930).

⁴⁸ C. L. Bickel and A. T. Peaslee, *J. Am. Chem. Soc.*, **70**, 1790 (1948).

⁴⁹ W. Meyerhoffer, *Berichte*, **37**, 2604 (1904).

the same solvent. With finite racemization X the system X - Y becomes pseudoternary, the components being Y , X_d and X_l . With complete, instantaneous racemization, it is again binary, with the components Y and X_r , but the diagram is no longer the same as that of Y with one of the optical isomers since the solubility of X_r will differ from that of an individual isomer in Y . Again, however, the system X - Y is binary, for any speed of racemization of X , if X_d and X_l form a solid solution of constant melting point and hence of constant solubility in Y , independent of the proportions of X_d and X_l in the system.

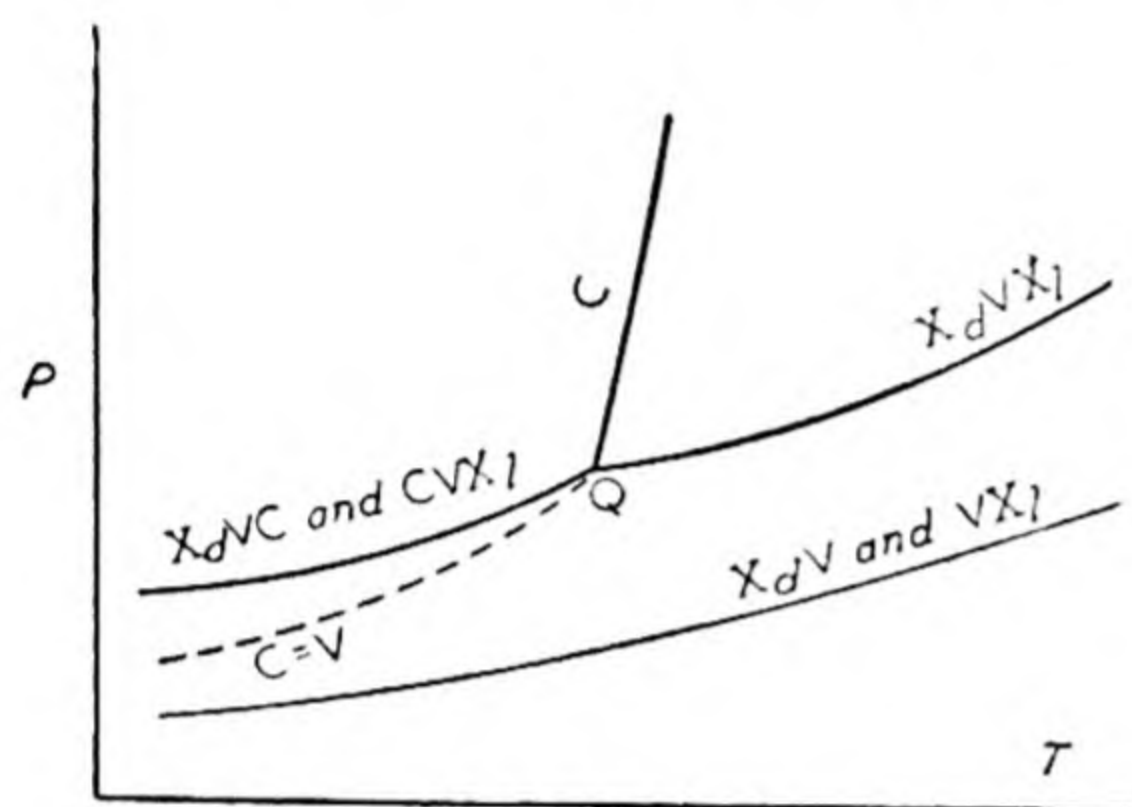


FIG. 7-56. Variation of Fig. 7-9, for optical isomers. For C , read X_dCX_l .

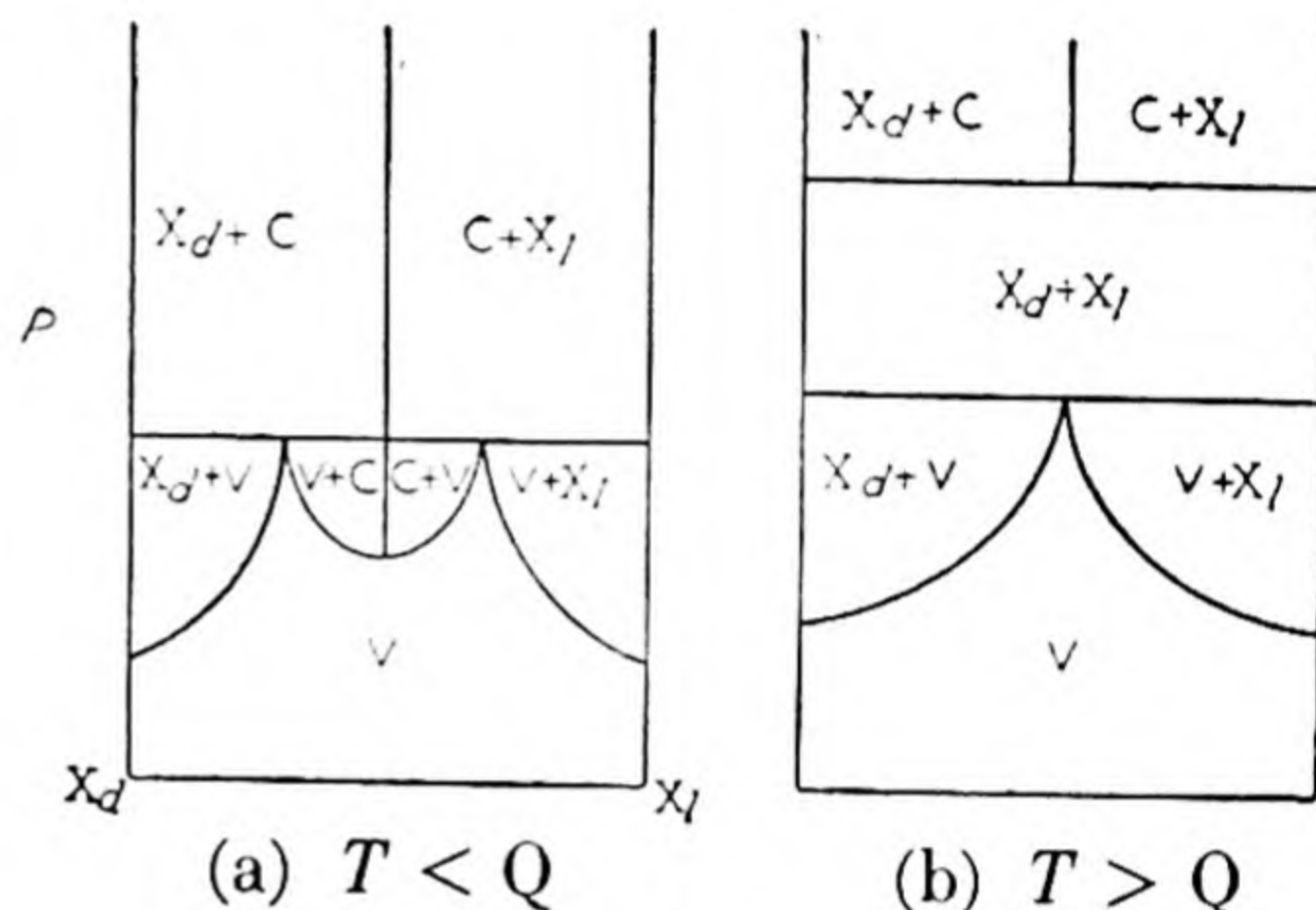


FIG. 7-57. Isotherms of Fig. 7-56.

3. A system consisting of an active form of one substance, such as X_d , and an active form of another, such as X'_d , is binary. But now we expect two phase diagrams: one (diagram *a*) for the two combinations $d + d'$ and $l + l'$, and another (diagram *b*) for the combinations $d + l'$ and $l + d'$. (We assume that d and l refer here to configuration, not merely to optical rotation.) While the solubilities of X_d in X'_d and of X_l in X'_l should be identical, as also those of d in l' and l in d' , the solubility of d in l' will not be the same as that of l in l' . If a binary compound is formed in diagram *a*, it will not be the same (in respect, for example, to melting point or to solubility in an inactive solvent Y) as a compound formed in diagram *b*, which may in fact not contain a compound at all. Such binary compounds, if both exist, are said to be related as diastereo-isomers. The *l*-menthyl esters of *d*-, *r*-, and *l*-mandelic acid, for example, melt at 98° ,⁵⁰ 83.7° ⁵⁰ and 77.6° ⁵¹ respectively. The difference between diagrams *a* and *b* may be pronounced when such binary compounds are involved, and the use of the difference between the compounds for the purpose of resolution of one of the substances is familiar. Theoretically the mere difference in solubility of the

⁵⁰ A. Findlay and E. M. Hickmans, *J. Chem. Soc.*, **91**, 905 (1907).

⁵¹ A. Findlay, Ref. G., *The Phase Rule and Its Applications*, Longmans, London, 1938, p. 137.

two forms of X in an active form of X' could also be used for resolution, but this becomes a problem of ternary systems.

It seems reasonable to expect, moreover, that if X_d is more (or less) soluble in X'_d than is X_l , the difference should remain of the same sign for the derivatives of X preserving the constitutional configuration of the original isomers X_d and X_l . A certain trend may possibly be expected in the difference between melting point diagrams, in respect to simple solubility or to compound formation, reflecting the fundamental difference in configuration between the two series of derivatives, when studied with a reference active (that is, asymmetrical) solvent or second component. When compounds are formed, this trend or difference seems to be a possible tool for the establishment of the configuration relationships of optically active substances, as shown by some work originally started by Timmermans.⁵² But when mere solubility differences are involved, the distinctions are generally experimentally beyond detection.

The effect of racemization of X in this system will be discussed in Chapter XIII, section C-6.

If the substance X contains more than one element of asymmetry, the complexity of its phase diagram, and hence of its phase relations with a second substance, such as Y or X' , increases. Not only is there now the possibility of a greater number of forms, but not all these forms are now identical thermodynamically. Thus tartaric acid, with two identical asymmetric carbon atoms, has two optically active forms, d - and l -, thermodynamically identical, melting at 170° , a racemic compound (inactive) of the two, with a higher melting point, 205° (and hence with lower solubility in some reference, inactive solvent), and an inactive meso-form, with internal compensation, melting at 140° .

⁵² Reviewed and expanded by A. Fredya, *The Svedberg (Memorial Volume)*, Almquist and Wiksells, Upsala, 1944, p. 261.

Chapter VIII Systems with Two Liquid Phases

A. The Equilibrium L_1L_2V

A miscibility gap in the liquid state is not to be expected in a binary system with continuous solid solution. We shall therefore assume pure solid phases, whether components or binary compounds; and the modification of the diagrams for some small extent of solid solution will be obvious.

The general properties of the MG in the liquid state, and its intersections with either the S/L or the L/V loop, have already been discussed in connection with Figs. 4-3 to 4-5. In those figures the liquid MG does not touch the "melting point" region, or the MG is "closed" at both ends for the system under its own vapor pressure or in the open (Fig. 4-9). In general, the closing of such a MG with increasing T and increasing P may be said to be expected on physical grounds. Thus the equilibrium L_1L_2V in the system isobutyl alcohol-water reaches the freezing point curves under the pressure of the system, but becomes closed, with a lower critical solution temperature (as $L_1 = L_2$ without vapor) as the pressure is increased, and the gap finally disappears entirely at high P^{1a} ; a similar case is the system methylethyl ketone-water.^{1b} The closing of the gap with falling T at ordinary P is, on the other hand, presumably the effect of chemical reaction or of "negative deviations" (chemical attraction) overcoming the expected increase in "positive deviations." This may be the effect in systems of amines and water, or nicotine-water; and in these cases the curve is usually rather abruptly flat, in T/c projection, at the lower consolute temperature, although always continuous, whereas the shape is usually relatively more rounded at an upper consolute temperature.² Fig. 8-1(a) is the system triethylamine-water, with a lower critical solution point K' at 18.5° , 30% amine,³ and Fig. 8-1(b) the system phenol-water, with an upper critical solution point K at 66° , 34% phenol.^{3, 4} Ac-

^{1a} J. Timmermans, *Arch. Néerland. Sciences exa. et mat.*, 6[III A], 147 (1923).

^{1b} P. Kohnstamm and J. Timmermans, *Proc. K. Akad. Wetensch. Amsterdam*, 15, 1021 (1913); see also Büchner (Ref. P), vol. II-2, p. 159.

² For thermodynamic considerations concerning the shape of the curve at the consolute point, see O. K. Rice, *Chem. Rev.*, 44, 69 (1949).

³ V. Rothmund, *Z. phys. Chem.*, 26, 433 (1898).

⁴ A. E. Hill and W. M. Malisoff, *J. Am. Chem. Soc.*, 48, 918 (1926); A. N. Campbell and A. J. R. Campbell, *ibid.*, 59, 2481 (1937).

according to the possible variations of the schematic relations of Fig. 4-3, it seems possible that either of the consolute points, upper or lower, may be either raised or lowered by increase of pressure. In actual observation, the lower consolute point seems always to be raised by increase of pressure, while both effects are known on upper consolute points.

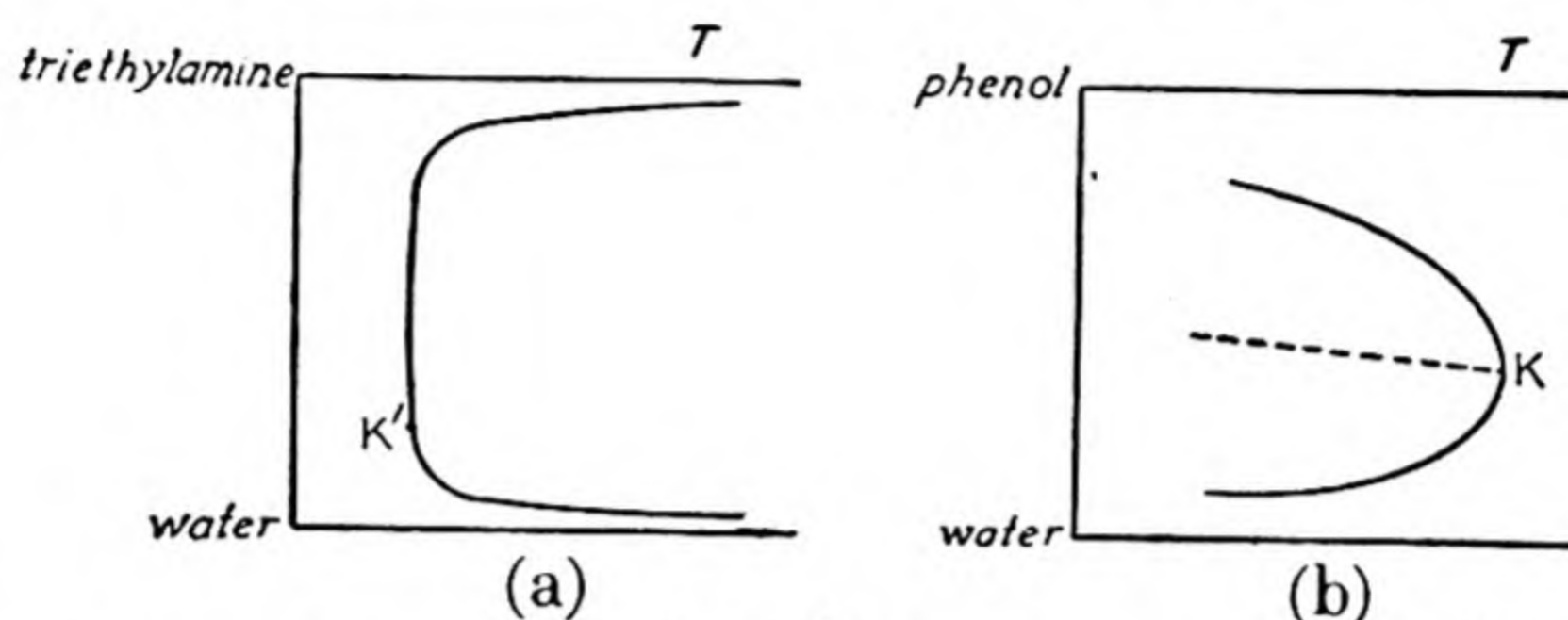


FIG. 8-1. Limited liquid miscibility: (a) triethylamine-water; (b) phenol-water.

The effect of variations in P on the observation of the upper critical solution phenomenon ($L_1 = L_2$, with V present) was discussed in Chapter IV. This consolute point, like all critical points, is also frequently very sensitive to the presence of impurities. While strictly a question of ternary or higher systems, this effect is usually measured as an estimation of the concentration of an impurity in the binary system. In the pure binary system the critical curve of the MG is a 3-dimensional curve in P, T, c ; in a ternary system, consisting of A, B , and a third substance, the impurity X , the critical curve at constant P is still a 3-dimensional curve, the variables being T and two composition terms, such as the ratio A/B and the percentage of X in the total. The curve will furthermore depend specifically on the nature of X , for a given binary pair such as aniline and water. If, then, the liquids aniline and water, one of them being impure, are taken in the ratio required to give the upper critical solution phenomenon for the pure liquids at atmospheric pressure and in the open, then, as in the effect of variation of P discussed in Chapter IV, we no longer expect in general to observe the critical phenomenon, since the proportions required will depend on the nature and the percentage of X . We shall, in general, observe the temperature merely of the appearance or disappearance of one of the two layers at constant (atmospheric) P .

Nevertheless this is called in practice the observation of the consolute temperature, as it is raised or lowered by the impurity X , in some proportion to its concentration. This is the Crismer test of purity of a liquid: if the critical proportions of A and B , using A known to be pure, do not give the consolute temperature expected at a certain pressure (atmospheric), B is impure, and the deviation is usually easily detected. The effect of any particular impurity is rather specific; but in general, if X is soluble (at the

given P and T) in both A and B to about the same degree, it is likely to increase the miscibility and hence lower the (upper) "consolute temperature," and it is otherwise expected to raise it.⁵ Thus KCl and naphthalene raise the critical solution temperature of phenol-water, while succinic acid and sodium oleate lower it. For the routine testing of the concentration of X in B, using pure A as the second liquid, the effect of X may be expressed as a molar elevation or depression of the consolute temperature. Some of these molar effects are extraordinarily high, compared to the effect of similar concentrations on the freezing point or boiling point of a substance,⁶ and hence prove useful for special analysis (determination of "aniline points," for example). They are also useful in "solubilizing" insoluble liquids, as in the effect of sodium oleate upon the system cresol-water.

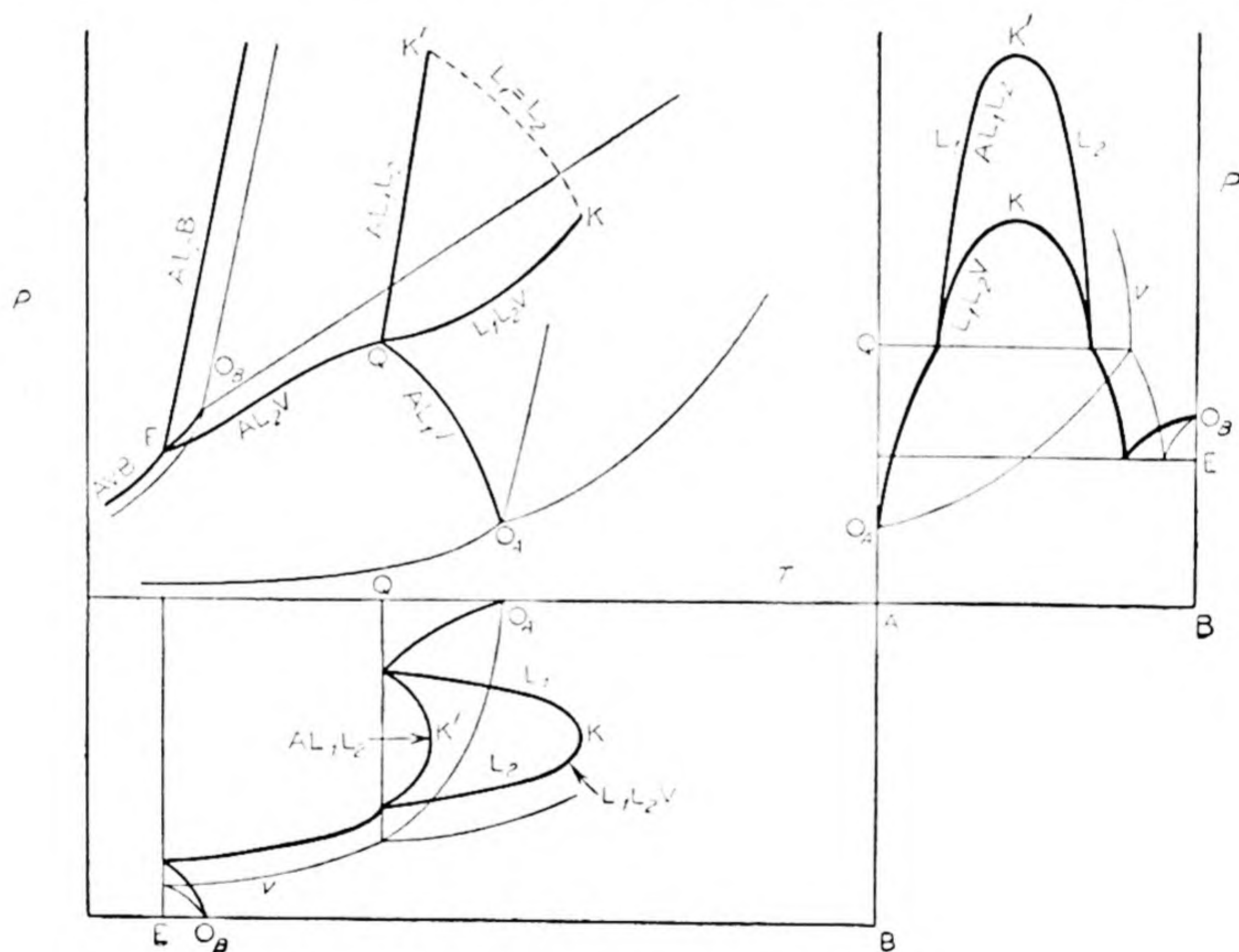


FIG. 8-2. The invariant point AL_1L_2V .

B. The Equilibrium AL_1L_2V

In Fig. 8-2, the liquid MG is shown intersecting both the AL and the LV equilibria (binary) including the ALV , that is, the melting point or solubility curve of A at the pressure of the system. In other words, the gap penetrates the solubility surface of A, including the curve ALV . The point Q, in P/T

⁵ J. Timmermans, *Z. phys. Chem.*, **58**, 129 (1907).

⁶ See, for example, the variation of the consolute point of the system phenol-water as a function of the proportion of deuterium oxide in the water; N. F. Hall, H. R. Wentzel, and T. Smith, *J. Am. Chem. Soc.*, **56**, 1822 (1934).

projection, is the intersection, then, of the L_1L_2V equilibrium, shown ending at an upper critical solution point K , with the solubility curve, ALV , of A , running from O_A to the eutectic E . It is therefore a quadruple, invariant point involving the phases AL_1L_2V and there rises from it, with increasing P , the equilibrium of the three condensed phases AL_1L_2 . The solubility curve of A is divided by Q into two parts, AL_1V from O_A to Q and AL_2V from Q to E .

The system water (A)–methylethyl ketone (B) may be cited as an example of Fig. 8-2, with Q at -8.5° , K' at -10° and 120 atm, K at 141° , and a pressure maximum on the curve $K'K$, at 85° and 1100 atm.^{1b} Another example, although not followed to point K , is the system menthol (A)–ethylene (B).⁷

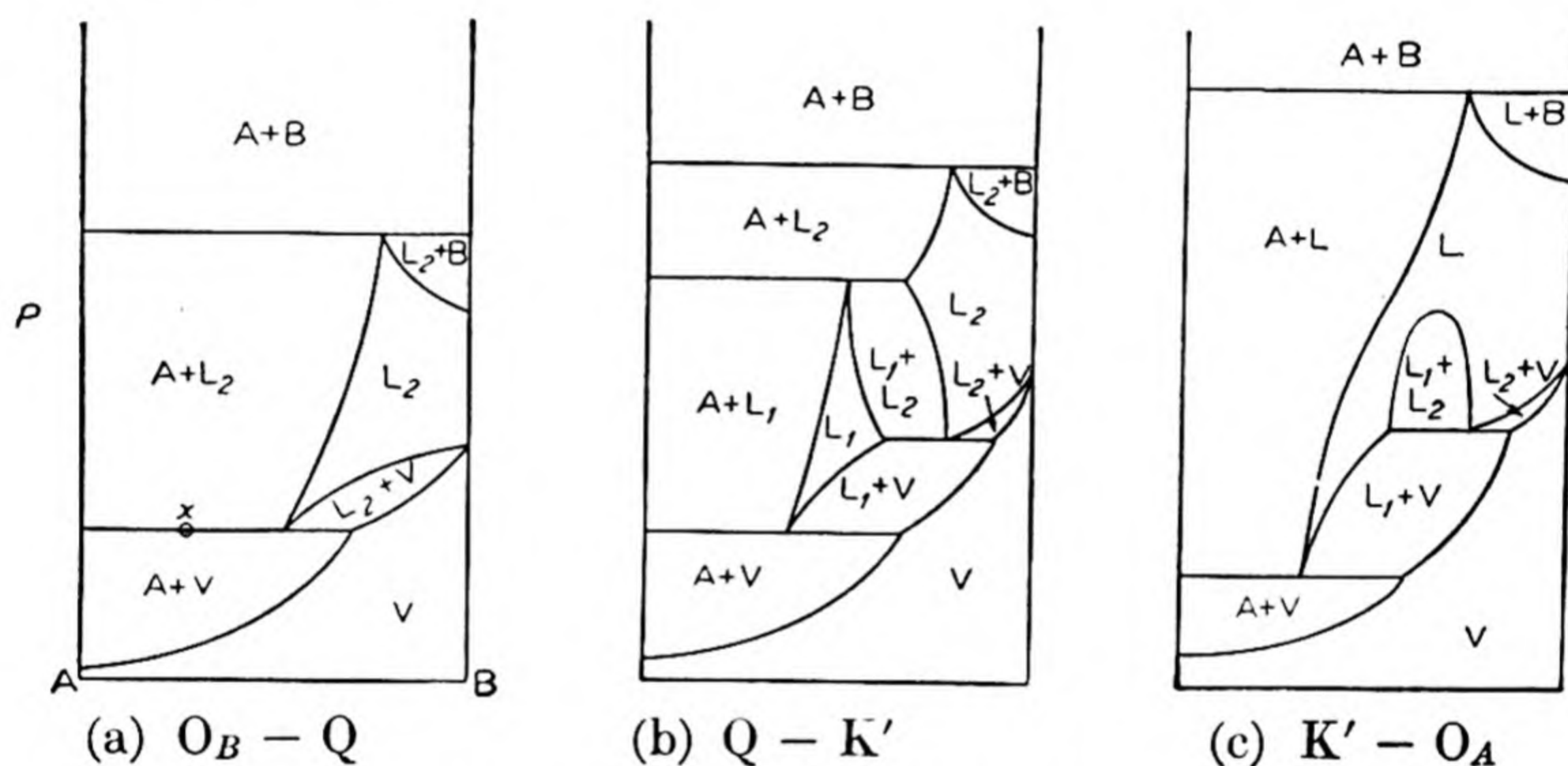


FIG. 8-3. Isotherms of Fig. 8-2.

The L_1L_2V equilibrium is assumed in Fig. 8-2 to be of Type I, that of Fig. 4-5(a), throughout; if it were of Type IV, as in Fig. 4-5(d), at Q , the composition of the vapor in the invariant equilibrium would lie between the liquids L_1 and L_2 , but would cross the L_2 curve before the point K is reached. For typical sections of Fig. 8-2, the isotherms are those of Fig. 8-3; the isobars, those of Fig. 8-4; as T rises above that of Fig. 8-3(a), a second liquid phase appears on the tie-line AL_2V , at a point such as x . This occurs at Q , and above this temperature (Fig. 8-3(b)), the equilibrium AL_2V no longer appears, and in its place there are the three equilibria AL_1L_2 , L_1L_2V , AL_1V , in descending P . In Fig. 8-4(a) the solubility curves AL_1V and AL_2V are represented by two tie-lines separated by the equilibrium $A + V$. As P increases, these meet at Q (Fig. 8-4(b)), and above this P (Fig. 8-4(c)), they are replaced by the tie-lines L_1L_2V and AL_1L_2 , representing the other two univariant curves meeting at Q . This assumes that Q is the pressure

⁷ G. A. M. Diepen and F. E. C. Scheffer, *J. Am. Chem. Soc.*, **70**, 4081 (1948).

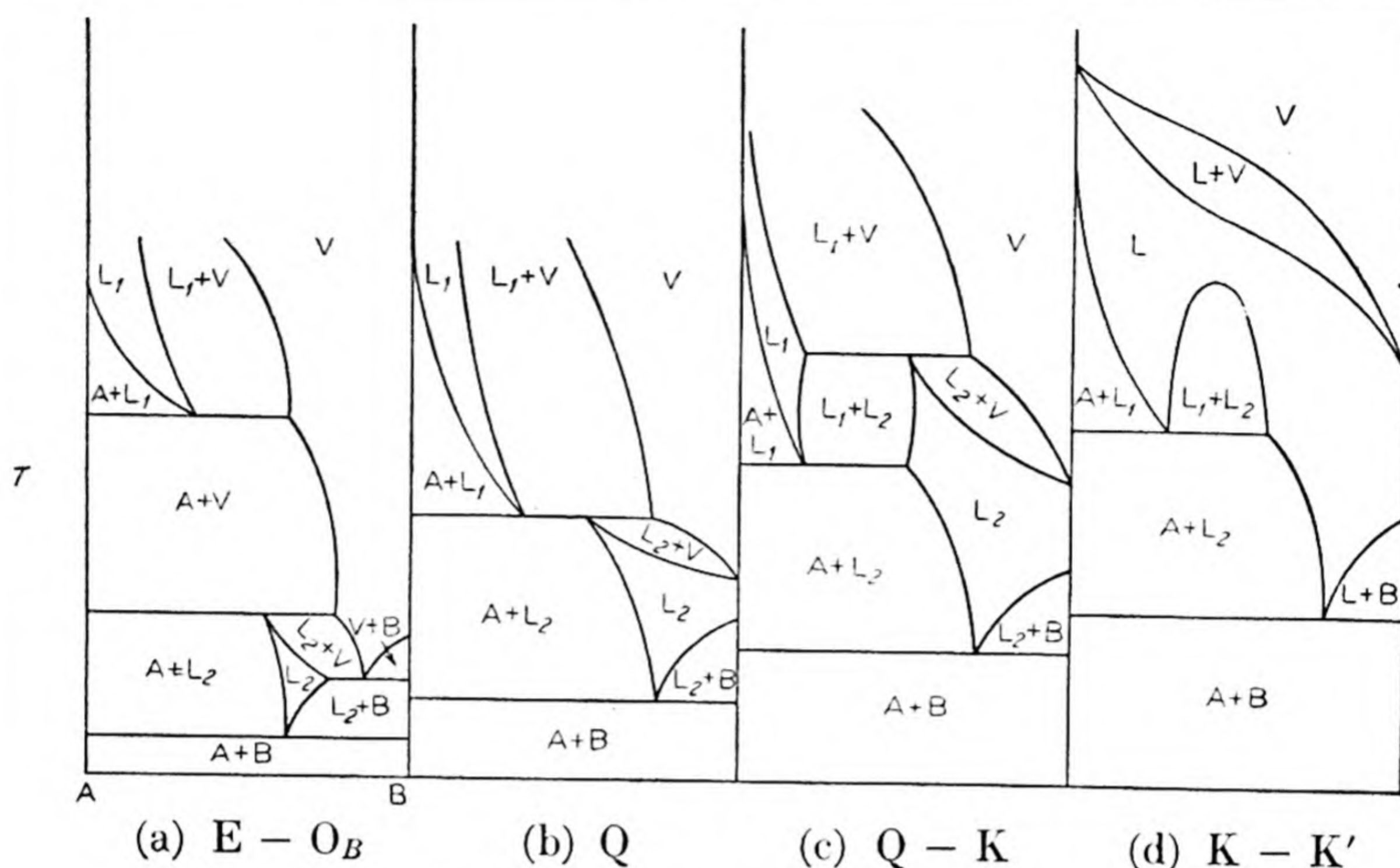


FIG. 8-4. Isobars of Fig. 8-2.

maximum in the solubility curve between E and O_A . If there is a maximum on either side of it, the changes in these isobars are not important. If the P/T slopes of the AL_1L_2 curve is negative rather than positive, so that $O_B < K' < Q$ in temperature, then the isotherms would appear as in Fig. 8-5, (a) and (b), in place of Fig. 8-3, (a) and (b). The isotherm between Q and O_A would still be as in 8-3(c)

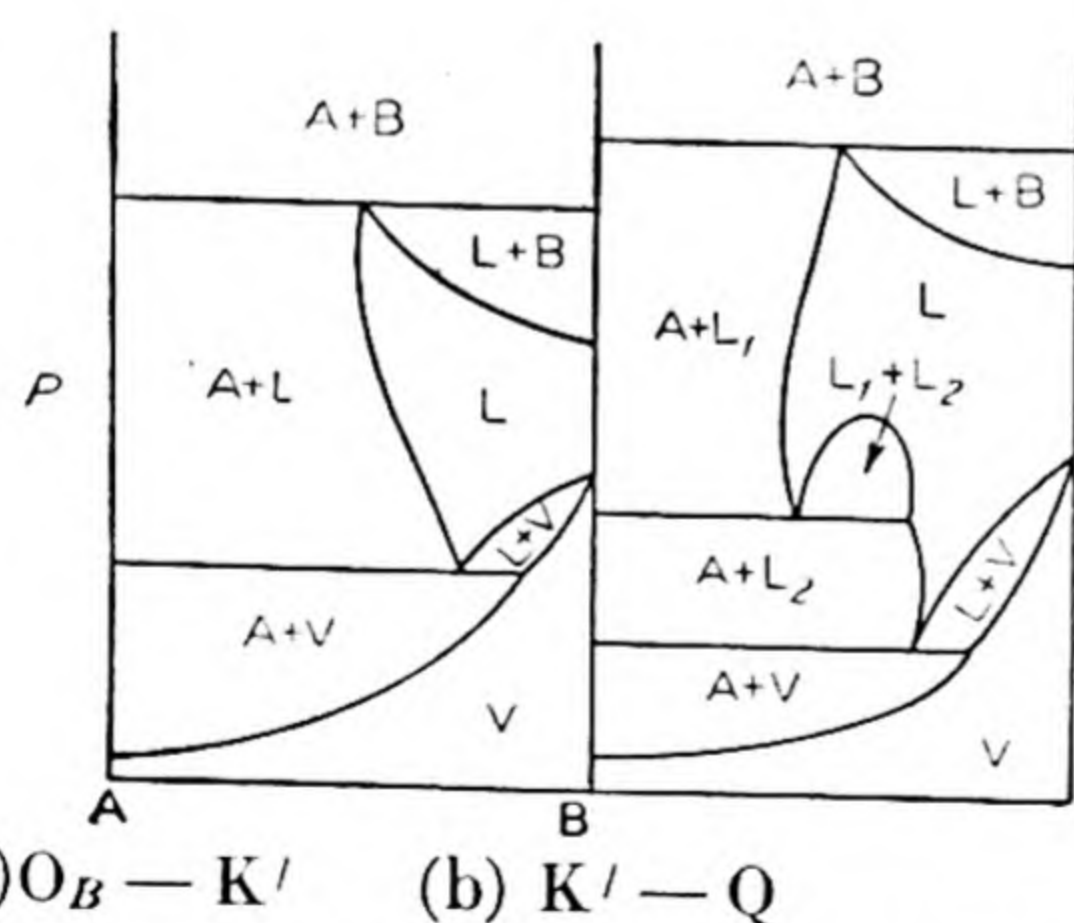
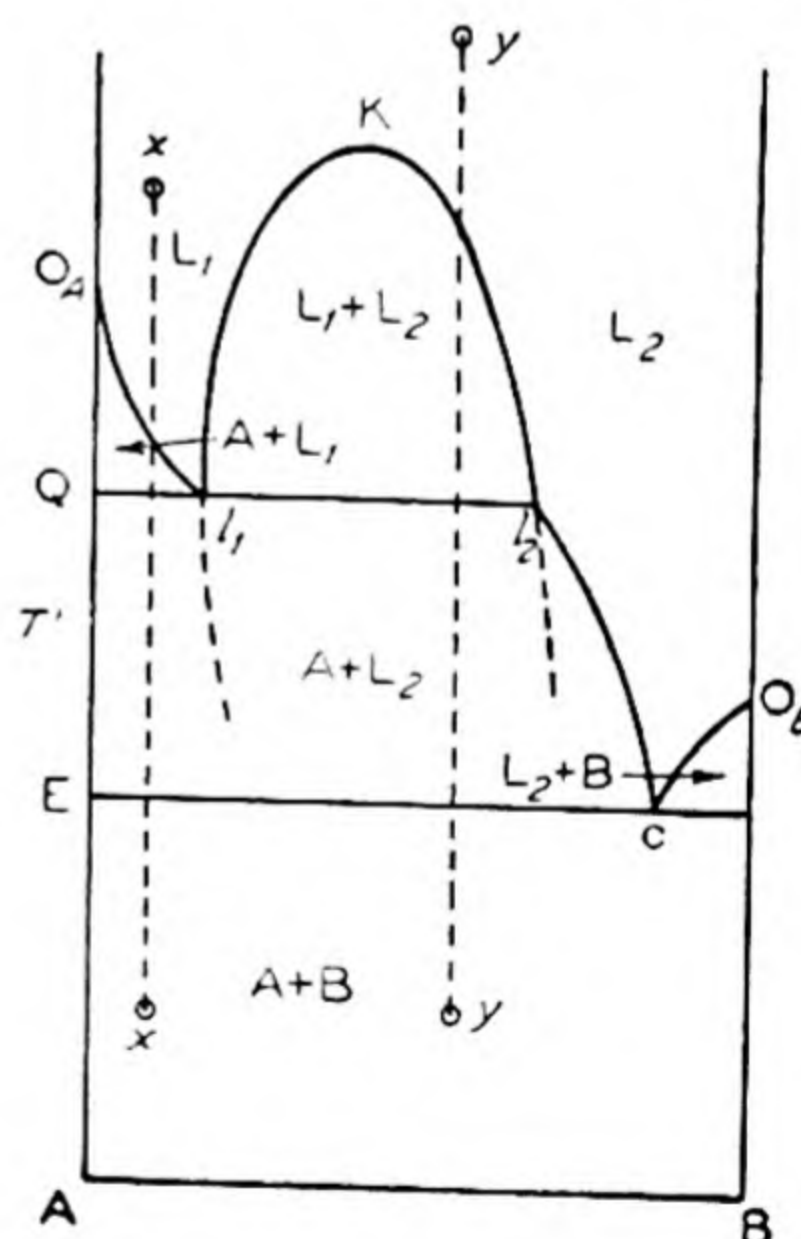
FIG. 8-5. Variation of Figs. 8-3(a) and 8-3(b) for negative slope of the AL_1L_2 equilibrium curve.

FIG. 8-6. Condensed diagram of Fig. 8-2.

As a "condensed diagram," the T/c projection of Fig. 8-2 becomes Fig. 8-6, with either slope of AL_1L_2 . Here K is the upper critical solution point, $L_1 = L_2 + V$, — let us say in open air — Q the open air invariant point AL_1L_2V , and E the usual eutectic. The point K may be higher or

lower than O_A and the MG may even be open at high T . The solubility curve of solid A is seen to be interrupted by the 2-liquid equilibrium and divided into two parts, $O_A l_1$ and $l_2 c$. The phenomena at constant T , such as at T' , present nothing new; addition of liquid B to solid A forms a solution on the curve $O_A l_1$, until the solid is all dissolved, and further addition of B to the solution causes the appearance of a second liquid, L_2 , when the total composition reaches the curve $l_1 K$, etc. If the liquid y is cooled, a second liquid, L_1 , appears when the curve $K l_2$ is reached, and the compositions and proportions of the liquids are given by the tie-lines within the MG , $L_1 + L_2$. When Q is reached the system becomes invariant (at atmospheric P), as solid A begins to precipitate. The temperature remains constant until the liquid l_1 is all consumed in the phase reaction $l_1 \rightarrow A + l_2 + \text{cals.}$ Then T falls again while the liquid composition follows the curve $l_2 c$, finally reaching the eutectic as a second invariant point. If the mixture x is heated, it begins to form the eutectic liquid at E, the system being invariant until solid B is all melted or dissolved, leaving $A + L_2$. The temperature then rises in the usual way as more A melts, until point Q is reached, and at this point the system is invariant while a second liquid, l_1 , forms, at the expense of A and l_2 . When the original liquid phase, l_2 , is all consumed, leaving $A + l_1$, T rises again and the solid is all melted when the curve $O_A l_1$ is reached. If the composition of the mixture falls between l_1 and l_2 , the solid all disappears at Q, leaving simply a 2-liquid system. The invariant point Q is therefore traversed by any mixture with composition between A and l_2 (ignoring vapor). The phase reaction $A + l_2 + \text{cals.} \rightarrow l_1$, especially if A is all consumed at the constant T , is known as "melting under the solvent." For the system benzoic acid-water, the temperatures of O_A , K, and Q are 121.4° , 116° , and 95°C , respectively;⁸ for succinic nitrile-water, 54.5° , 55.5° and 18.5° , respectively.⁹ In the system Ni-Ag there is a similar liquid MG on the freezing point curve of Ni, and at the same time the solid phase contains some Ag in solid solution.¹⁰

The liquid-liquid system may sometimes be supercooled with respect to the solubility curve of A, giving the metastable extensions shown as dotted lines. With precipitation of A, such a system, of course, reverts to $A + L_2$, the liquid having a composition on the curve $l_2 c$. It is even possible for the $L_1 L_2 V$ system to be supercooled to such a point as to give rise to a metastable quadruple point, Q' , involving the solubility curve of B, with the phases $L_1 L_2 V B$, as in Fig. 8-7. Such relations have been assumed in explanation of the solidification of certain silicate-sulfide systems involving

⁸ N. V. Sidgwick and E. K. Ewbank, *J. Chem. Soc.*, **119**, 979 (1921).

⁹ F. A. H. Schreinemakers, *Z. phys. Chem.*, **23**, 417 (1897).

¹⁰ Hansen, *op. cit.*, p. 43.

two liquid layers, and in which one component, silica, has a marked tendency for super-cooling to the "vitreous" condition.¹¹

If the solubility of A decreases with rising T , as in Figs. 5-2(a) and (b) in Chapter V, it becomes possible for a 2-liquid area with a lower consolute point to impinge upon the solubility curve, as in the system KI-SO₂ shown (schematically) in Fig. 8-8, as the usual T/c projection of the condensed phase relations at the pressure of the system.¹²

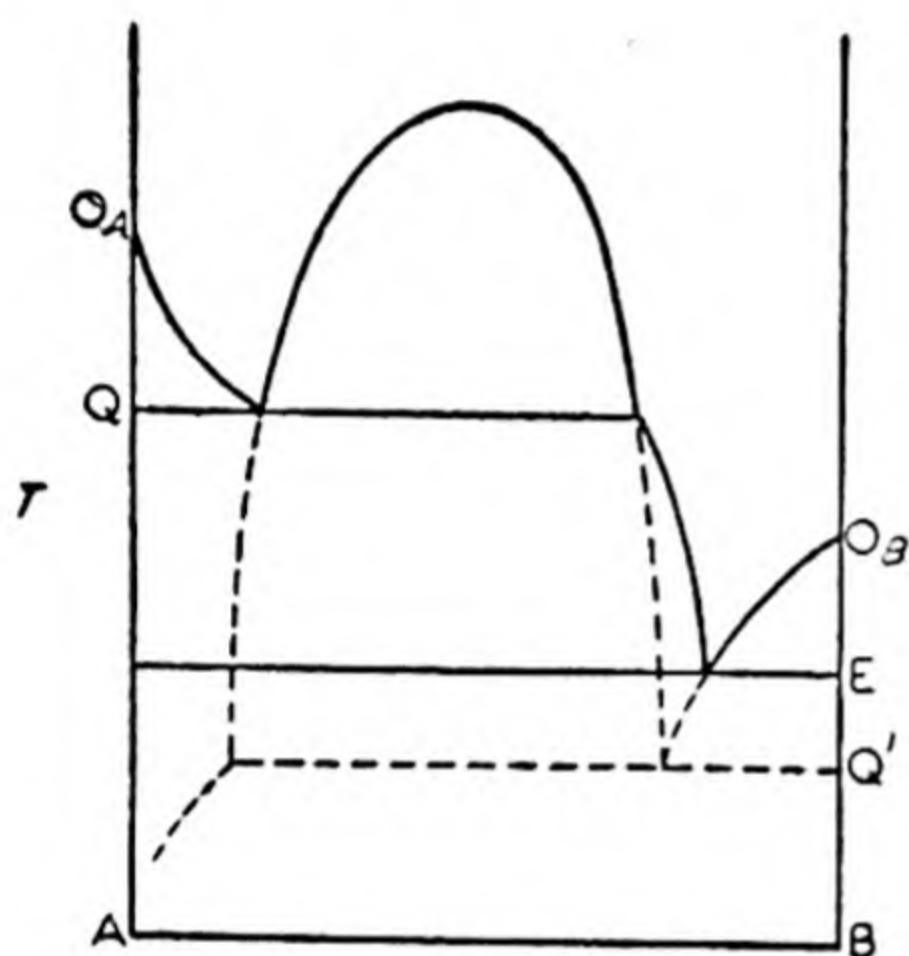


FIG. 8-7. Metastable invariant point, L_1L_2VB .

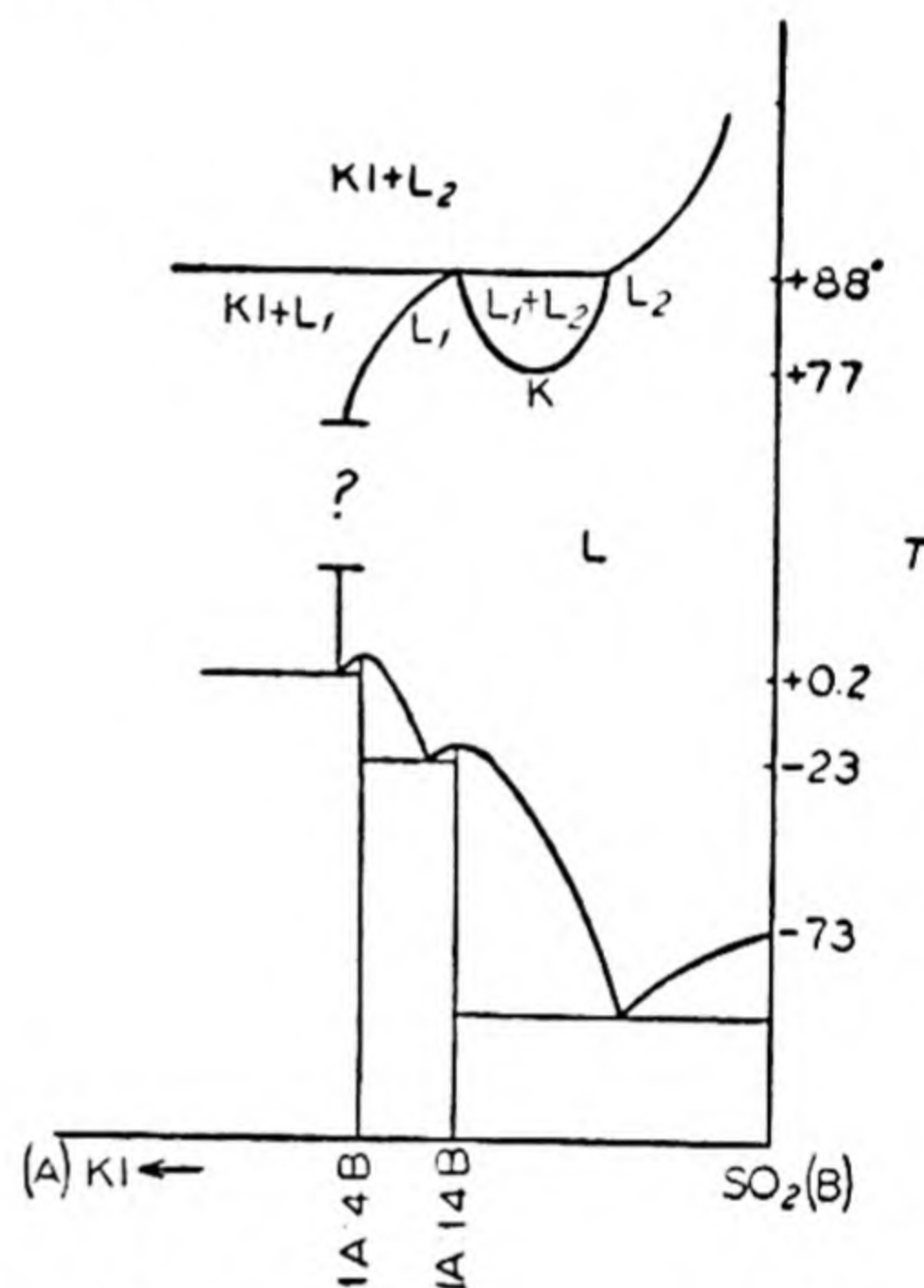


FIG. 8-8. Part of system KI-SO₂ (condensed diagram, schematic).

C. Submerged Miscibility Gap

In some cases the solubility curve of A is continuous, the components being completely miscible in the liquid state at the freezing point curve, but if the liquid is supercooled with respect to A, it may split into two liquid layers, indicating a "submerged" or metastable MG lying completely below the solubility curve of A. When this MG is close to the solubility curve, its presence may be suspected from the typical S shape of this curve (Fig. 8-9). This S-shaped solubility curve or highly flattened freezing point curve is to be expected on thermodynamic grounds in such circumstances. In Fig. 8-10 the molar free energy G at constant P of the liquid phase (continuous curve from A to B) is plotted against mole fraction, together with that of solid A, for supposedly equal increments (+ or -) of T . The solubility of A is, of

¹¹ R. Vogel (Ref. V), pp. 272-274; referring to the experimental observations of J. Vogt, *Die Silikatschmelzlösungen*, Kristiania, 1904.

¹² P. Walden and M. Centnerszwer, *Z. phys. Chem.*, **42**, 432 (1903). As indicated in Fig. 8-8, some parts of the system as reported by these authors are not clear; nor are the formulas of the two solid compounds certain.

course, given by the tangent from G_A to the liquid curve. As the MG in the liquid state is approached with change of T , the liquid curve becomes flattened, preparatory to developing two minima, the condition for separation into two liquid layers. As a result the rate of change of the solubility s , with respect to T , becomes very high in the vicinity of the MG . If the MG just touches the solubility curve, the tangent from G_A touches the liquid curve just where it first develops a maximum and two minima. If the MG is stable, part of it lying above the solubility curve in the T/c plot

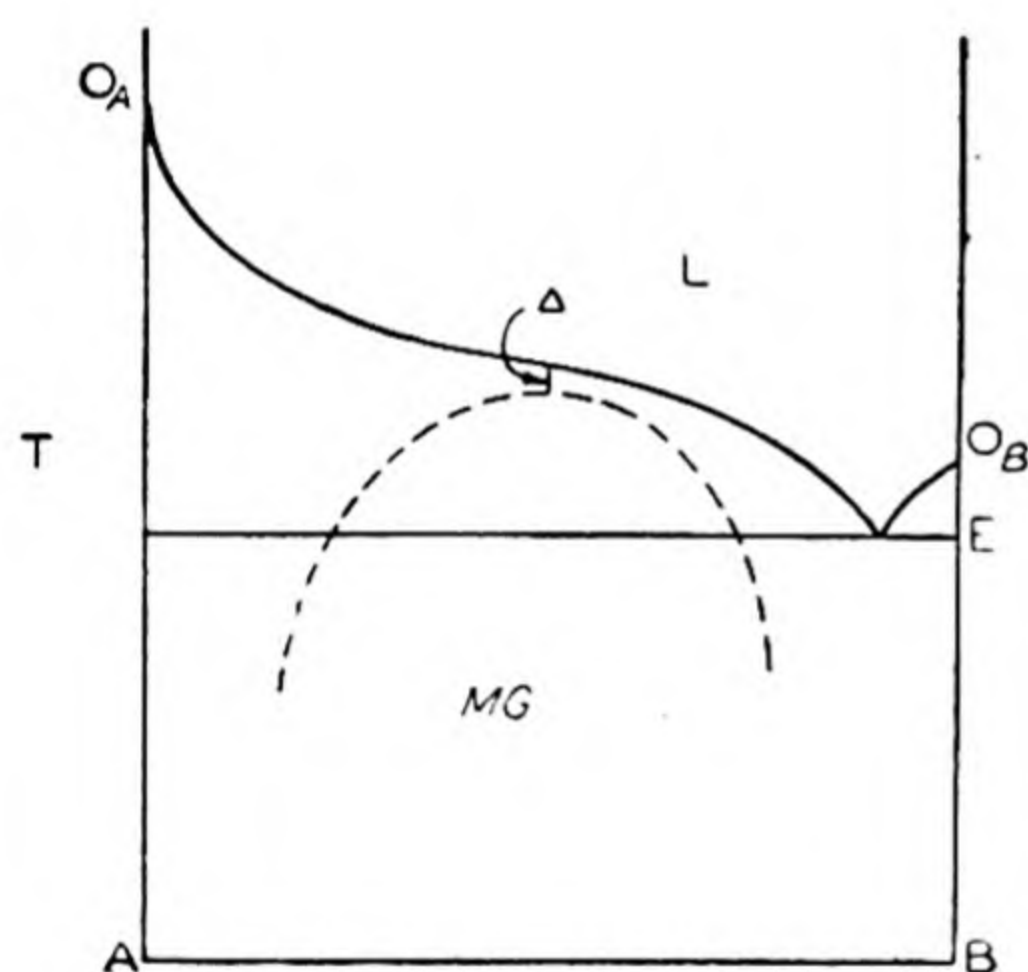


FIG. 8-9. "Submerged" miscibility gap.

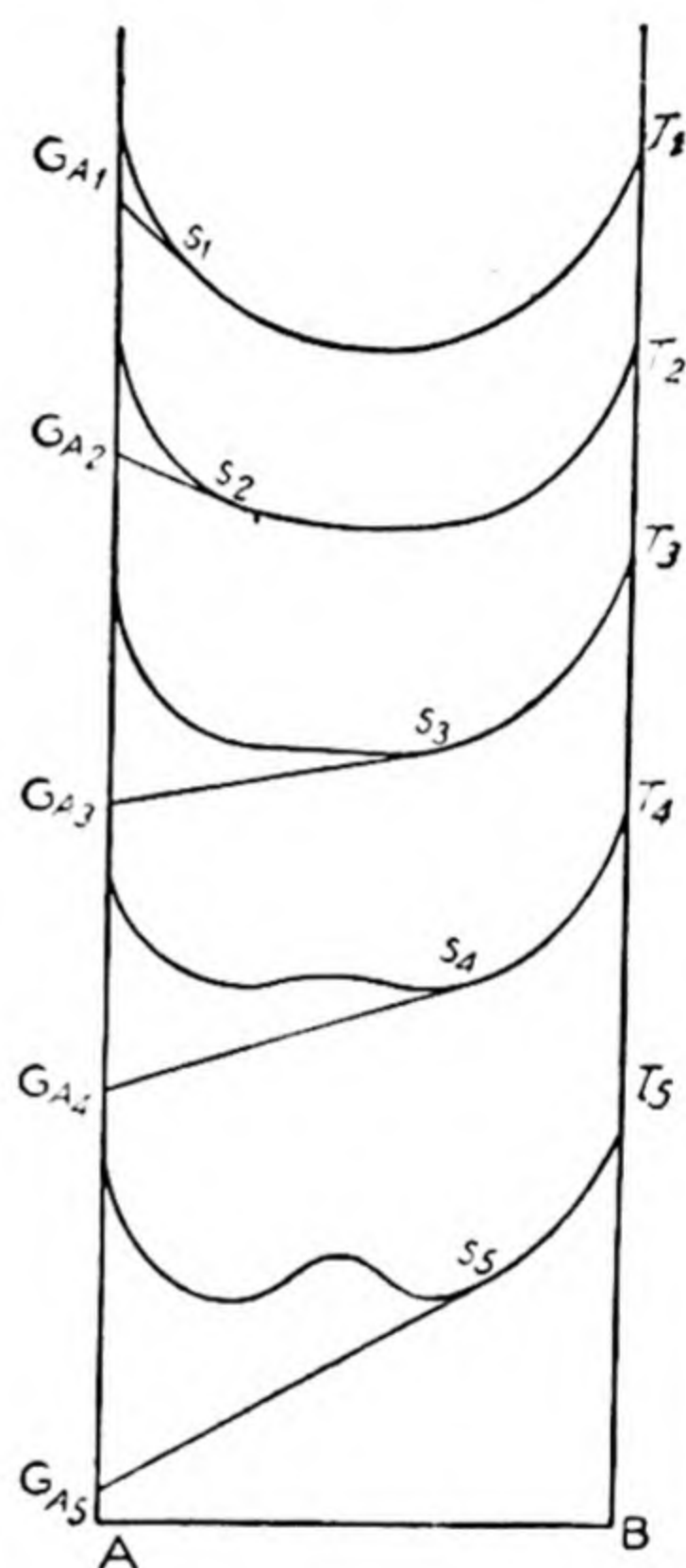


FIG. 8-10. Isobaric isotherms of free energy for submerged miscibility gap; at each temperature G is plotted vertically against c , or proportion of A and B.

of Fig. 8-9, the two minima first appear on the right of s in Fig. 8-10, and there will accordingly be a 3-phase equilibrium for the phases A, L_1 and L_2 when the tangent is common to both minima. If the MG lies entirely below the solubility curve (metastable or submerged MG as in Fig. 8-9), the two minima will first appear on the left of s . In this case, then, the curve of s against T tends to be S-shaped, with a flat portion in which ds/dT approaches ∞ , and $= \infty$ at a critical solution point such as point K' of Fig. 8-2 (a singular point).

The system salicylic acid-water is an example, with an S-shaped solubility curve for salicylic acid and a submerged 2-liquid system detectable on super-cooled liquid.⁸ In such cases the critical solution temperature of the sub-

merged MG may be estimated directly upon the supercooled liquid or by extrapolation of the effect of a third component,¹³ such as sodium chloride on the critical solution temperature of the system water-organic liquid. Such studies indicate a rough proportionality between the flattening of the solubility curve and the closeness of the MG . In a series of "homologous" or related systems (the solvent B constant, the A component being varied as a series of related compounds), the derivative ds/dT at the inflection point of the solubility curve is roughly inversely proportional to the distance Δ in Fig. 8-9, between the submerged critical solution temperature and the flat portion of the solubility curve. The proportionality constant, or the product $(ds/dT) \Delta$, $\cong 330$ for a number of systems of substituted benzoic acids with water as solvent,^{13b} and $\cong 190$ for the same acids with benzene or heptane as solvent.⁸

A liquid MG is found on the freezing point curve of SiO_2 in the binary systems with the oxides of Mg, Ca, Sr, Zn; in the system BaO-SiO_2 the solubility curve of SiO_2 is not broken by a 2-liquid area, but one may suspect the nearness of a MG from the shape of the curve.¹⁴

D. The Equilibrium AL_1L_2B

It should be possible, at high P , for the MG , whether or not it intersects the solubility curve EO_A , to impinge on both the freezing (or solubility) surface of A and that of B (Fig. 8-11). Since these relations do not involve

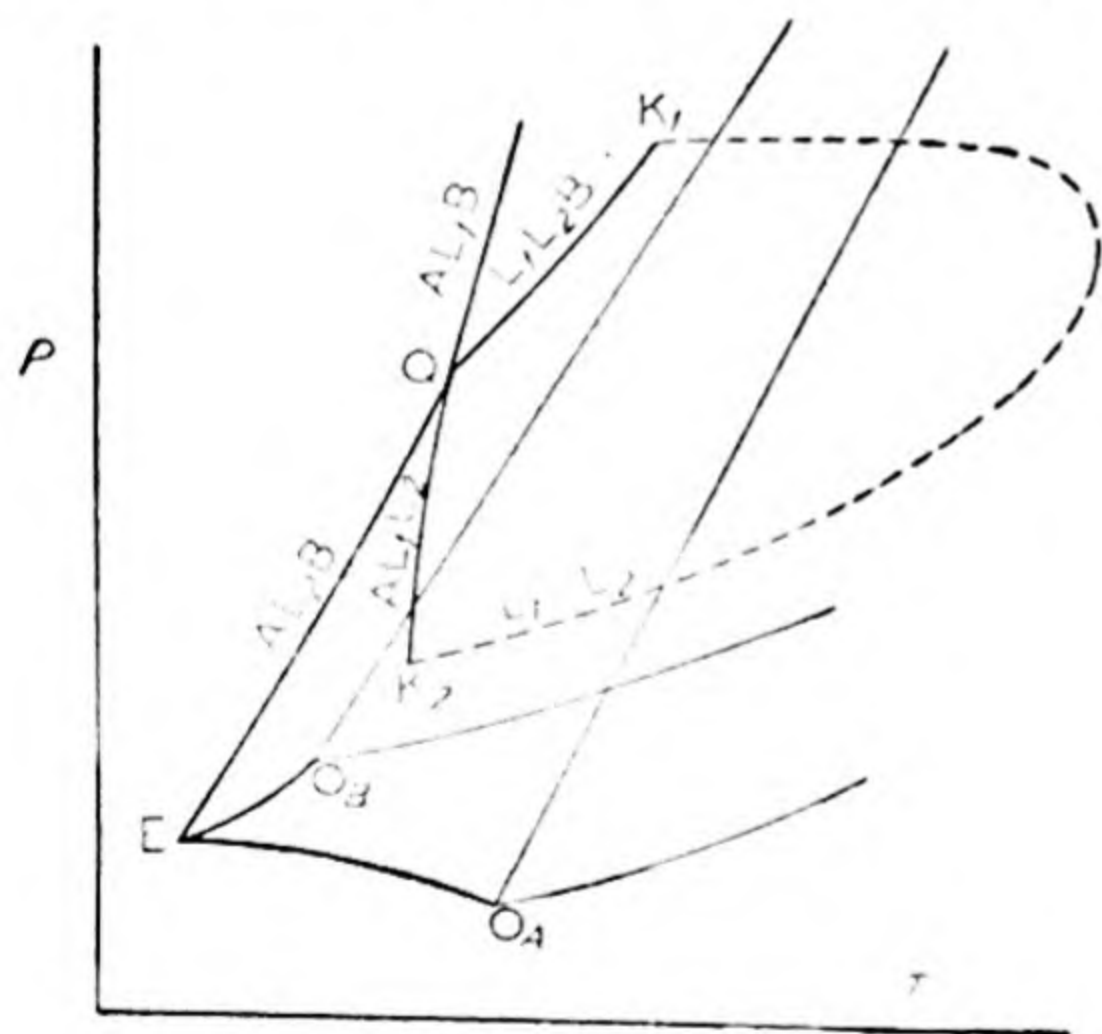


FIG. 8-11. The invariant point AL_1L_2B .

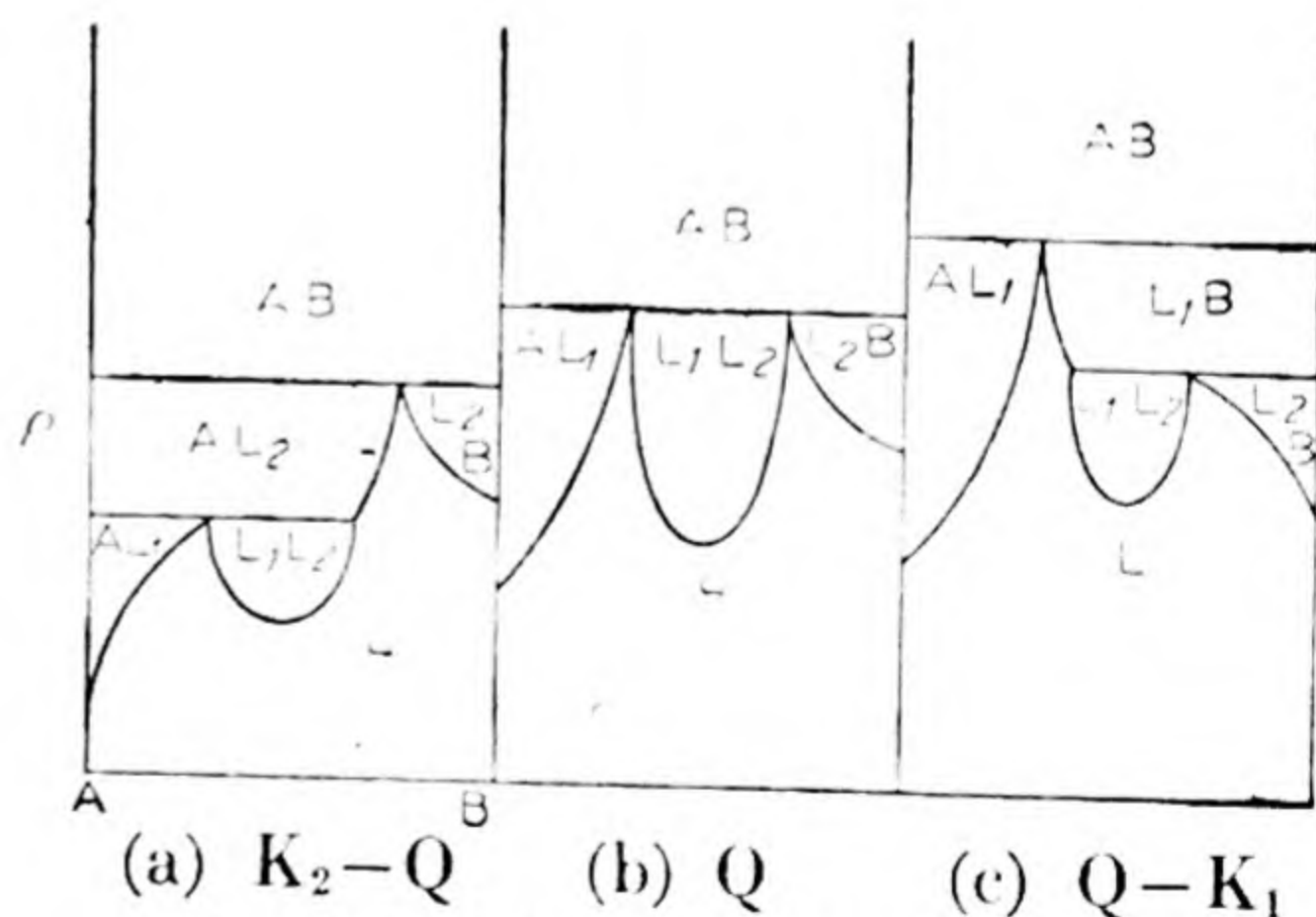


FIG. 8-12. Isotherms of Fig. 8-11.

the vapor, it has been assumed, for simplicity, that the MG does not penetrate the L/V loop. Above the point Q, the MG is shown intersecting the solubility surface of B, the L_1L_2B equilibrium ending at the critical solution

¹³ (a): O. Fleischner and I. G. Rankin, *Sitzungsber. K. Akad. Wiss. Wien*, **118**, II b, 695 (1909); (b): O. Fleischner, *J. Chem. Soc.*, **95**, 668 (1909). ¹⁴ I. C. T., IV-86.

point K_1 ; below Q it impinges on the solubility surface of A , the AL_1L_2 equilibrium ending at the critical solution point K_2 . At Q these two 3-phase equilibria meet, where the MG shifts from one surface to the other, and they there intersect the eutectic curve AL_2B (cf. Fig. 8-2); the eutectic curve above Q now involves the "A-rich" liquid and is therefore marked AL_1B . Q is therefore an invariant, quadruple point for the phases AL_1L_2B . The pertinent isothermal relations near the point Q are shown in the sections of Fig. 8-12; the isobars would be of the same general form, turned upside down.

E. The Equilibrium CL_1L_2V

The MG may intersect the solubility curve of a binary compound just as well as that of a component, but ordinarily this introduces nothing new. The MG in the system phenol-water intersects the solubility curve of the hemihydrate of phenol (Fig. 8-13, schematic, condensed diagram). This hydrate has a congruent melting point, but its solubility curve, from its

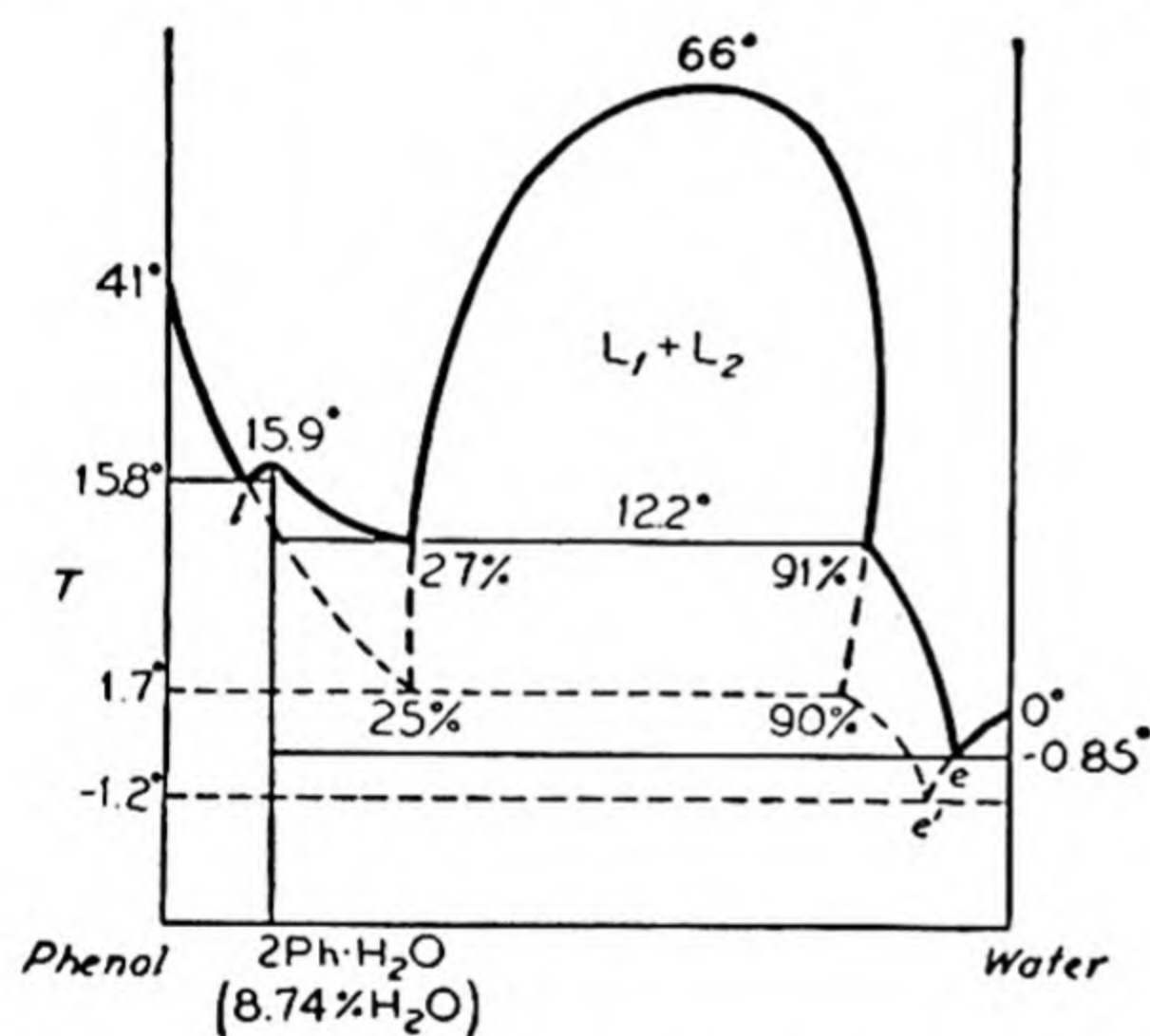


FIG. 8-13. System phenol-water; % H_2O = 8.25 at point l , 95 at point e , 93.5 at point e' .

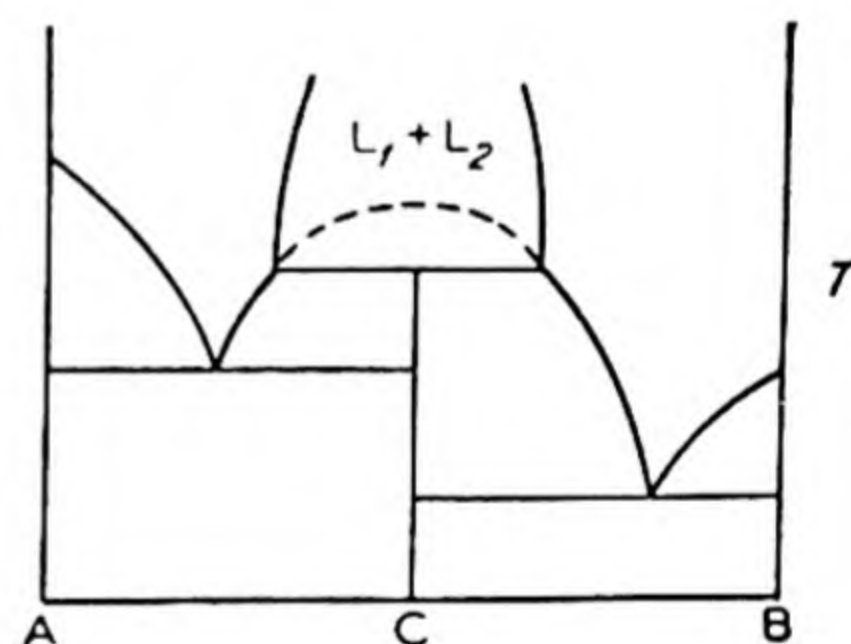


FIG. 8-14. Compound melting to two liquids.

congruent melting point to the eutectic with ice, is interrupted by the 2-liquid area, with a quadruple point for the hydrate + two liquids (+ vapor) at 12° . These relations are shown in the full curves of Fig. 8-13. But the hydrate is made to crystallize only with difficulty, and the system is usually observed in its metastable relations (dotted curves of Fig. 8-13). When the 2-liquid system is supercooled with respect to the hydrate, a metastable quadruple point, involving solid phenol, is obtained, at 1.7° , and below it a metastable eutectic, at -1.2° , involving phenol and ice.¹⁵

In the system $HCl-H_2O$ there are three congruently melting hydrates,

¹⁵ F. H. Rhodes and A. L. Markley, *J. Phys. Chem.*, **25**, 527 (1921).

HCl·1, 2, 3H₂O, and a liquid miscibility gap impinging on the HCl side of the freezing point curve of the monohydrate, very close to its congruent melting point, at the pressure of the system.¹⁶

In the system methyl iodide–pyridine, the freezing point curve of the very stable 1:1 compound has a liquid *MG* on each side of its congruent melting point — which, however, may in this case even be a true triple point, so that the two miscibility gaps may pertain to different binary Systems.¹⁷

F. The Equilibrium L_1CVL_2 (or L_1CL_2V)

Finally, the *MG* may engulf the congruent melting point of a binary compound, resulting in the schematic relations shown in Fig. 8-14 (condensed diagram). The melting point of the compound, presumably at the pressure of the system itself, is now metastable, lying within a 2-liquid area or *MG* which has penetrated the “intersection curve” (see Chapter VII, Fig. 7-34) of the binary compound, engulfing its congruent melting point. Such a compound is said then “to melt to two liquids,” or better, to decompose into two liquids.

The schematic relations for a system in which a binary compound decomposes into two liquids are shown in Fig. 8-15. This figure is to be compared with both Figs. 7-34 and 8-2. The *MG* is outlined, in P/T projection, as in Fig. 8-2, by the L_1L_2V curve, running from Q to K , the upper critical solution point, and by the consolute curve, $K'K$. The L_1L_2V relations are assumed to be of Type IV at the point Q , with the vapor composition between the two liquids, but of Type I or III at higher T , the vapor composition crossing the L_2 curve at point m' , as shown in the T/c and P/c projections. (A similar crossing is assumed to occur at point m , between the solubility curve of the compound and the azeotropic minimum of the L/V loop, so that the order of the phases between E_2 and Q changes there from CL_2V to CVL_2 ; point m therefore corresponds to N in Fig. 7-47.)

The *MG* impinges on the freezing surface of the compound from point K' , the critical solution point CL_1L_2 with $L_1 = L_2$ in composition, to the quadruple point Q , which is on the “intersection curve” of the compound (E_1E_2 of Fig. 7-34). The contact at K' is not on the congruent melting curve ($C = L$) of the compound, for, as explained in Chapter IV, such a contact, between a critical curve ($K'K$) and a 2-phase equilibrium, is not expected to occur on a maximum or minimum of the latter. It is here assumed to occur on the B side of the composition C , giving rise to the 3-phase

¹⁶ F. F. Rupert, *J. Am. Chem. Soc.*, **31**, 851 (1909).

¹⁷ A. H. W. Aten, *Z. phys. Chem.*, **54**, 124 (1906).

equilibrium CL_1L_2 , the curve running from K' to point R . As P falls, the contact between MG and solubility surface widens, or the L_1 - L_2 portion of the tie-line CL_1L_2 lengthens, until a point is reached when L_1 has the composition C . This is the point when the congruent melting curve $C = L$ enters the MG and is therefore marked as a singular point, type m , or point R . Below this point, the order of the three phases changes to L_1CL_2 , so that the solubility curve CL_1L_2 from K' to R becomes a *decomposition* curve,

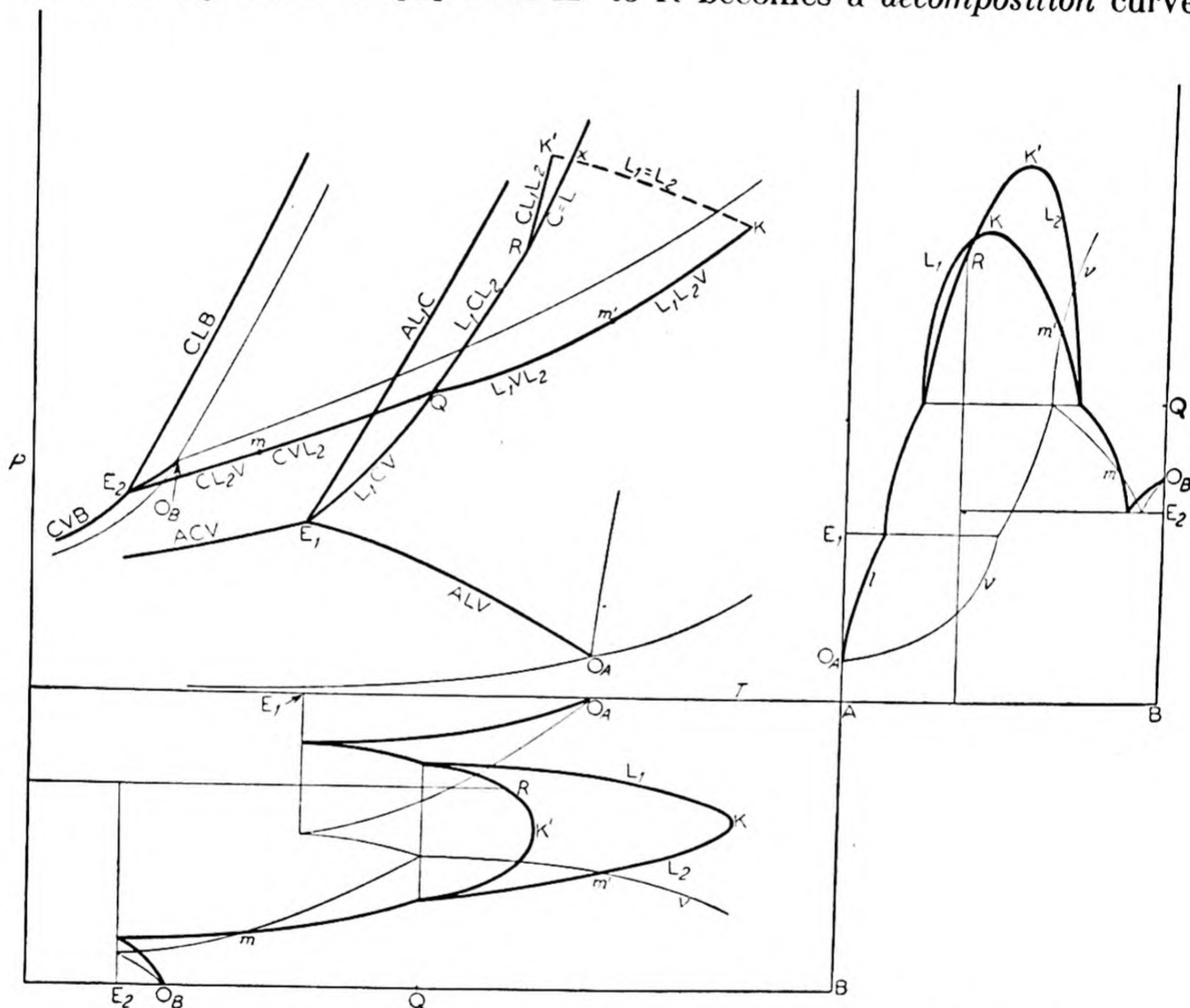


FIG. 8-15. $P/T/c$ relations for compound melting to two liquids.

L_1CL_2 from R to Q . Point Q , unlike point M of Fig. 7-34, is a true invariant, quadruple point, involving the phases L_1CVL_2 (or L_1CL_2V if the L_1L_2V relations are other than type IV). It is the intersection of four 3-phase univariant equilibria: the L_1VL_2 curve of the MG , the solubility curve of the compound, E_2Q , and two decomposition curves, L_1CL_2 (QR) and L_1CV (QE_1 , which is the remnant of the curve ME_1 of Fig. 7-34, cut down by the MG).

The plane of the compound, considered open at high P and low T , is now bounded by the congruent melting curve $C = L$ to point R , the decomposi-

tion curve L_1CL_2 from R to Q , the decomposition curve L_1CV from Q to the incongruent eutectic E_1 , and the decomposition curve ACV below E_1 . Some isotherms and isobars are shown in Figs. 8-16 and 8-17.

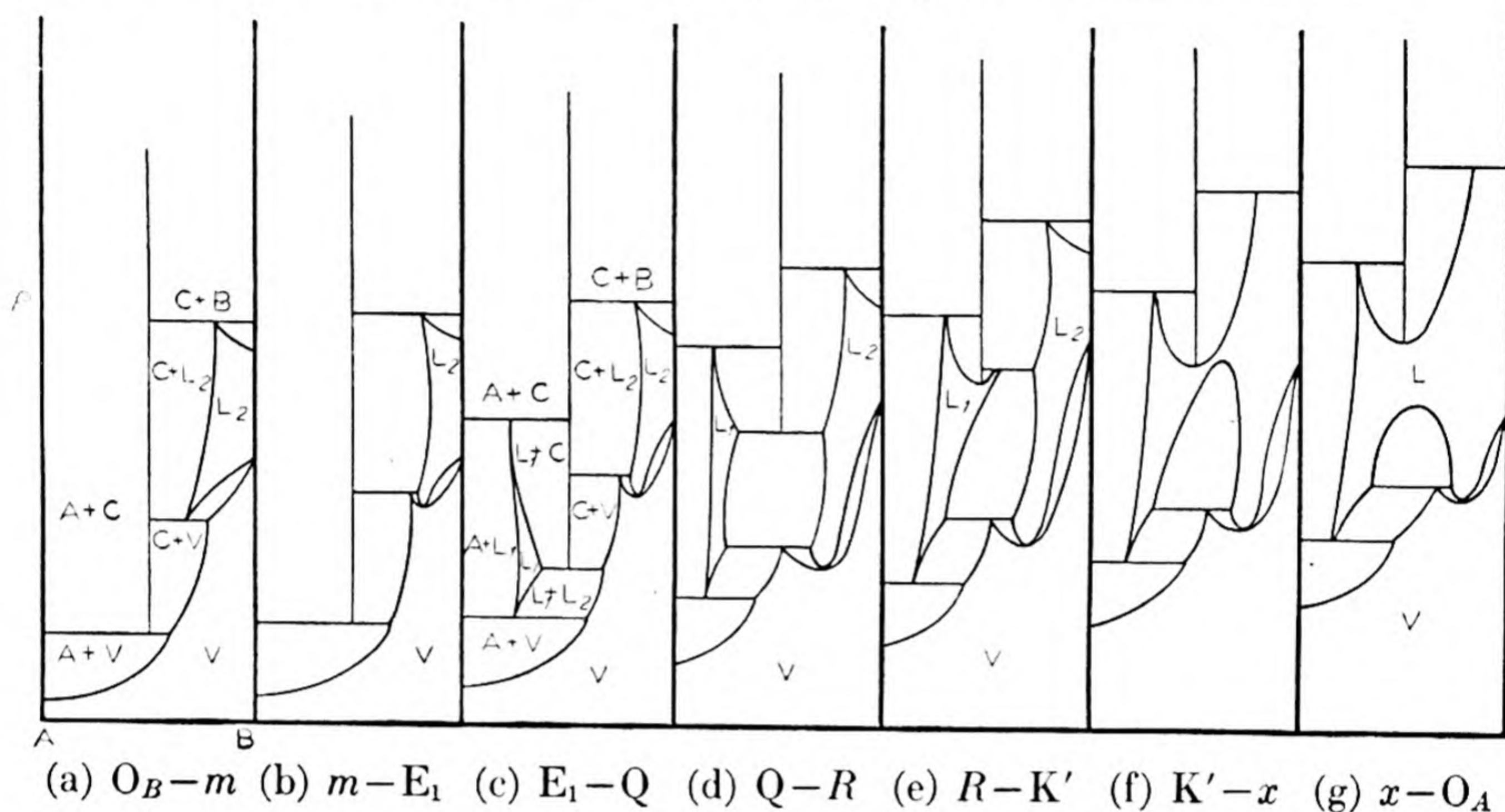


FIG. 8-16. Isotherms of Fig. 8-15.

For examples of binary compounds decomposing in this fashion into two liquids, we may mention CaCd_2 (β modification) at 685° ¹⁸, LaMg_3 at 766° ¹⁹ and $\text{H}_2\text{S} \cdot 5\text{H}_2\text{O}$ at 29.5° and 22.1 atm pressure.²⁰

G. Critical Phenomenon ($L = V$)

We shall now consider the case in which the liquid MG intersects the critical ($L = V$) curve K_AK_B of the system. In this case there may be a lower critical solution (consolute) point for the equilibrium L_1L_2V , as shown at point K_1 of Fig. 8-18, but not an upper consolute point, since the MG remains open up to the critical region. If, of course, as in the preceding sections, the L_1L_2V equilibrium reaches a freezing point surface, the curves $L_1 = L_2$ and L_1L_2V remain apart and there is no lower critical solution point K_1 . It will be assumed, also, that the SLV (solubility of solid) curves do not reach the critical curve K_AK_B ; such intersection was discussed in Chapter V.

When the MG intersects the critical curve, there will be a **critical end-point**, K_c , where the L_2 branch (on the side of the vapor, and hence, in general, of the more volatile component B) crosses the curve running from K_B to K_A . At K_c , a singular point of type k , the phases L_2 and V become

¹⁸ Hansen, *op. cit.*, p. 393.

¹⁹ *Ibid.*, p. 844.

²⁰ F. E. C. Scheffer, *Z. phys. Chem.*, **84**, 734 (1913).

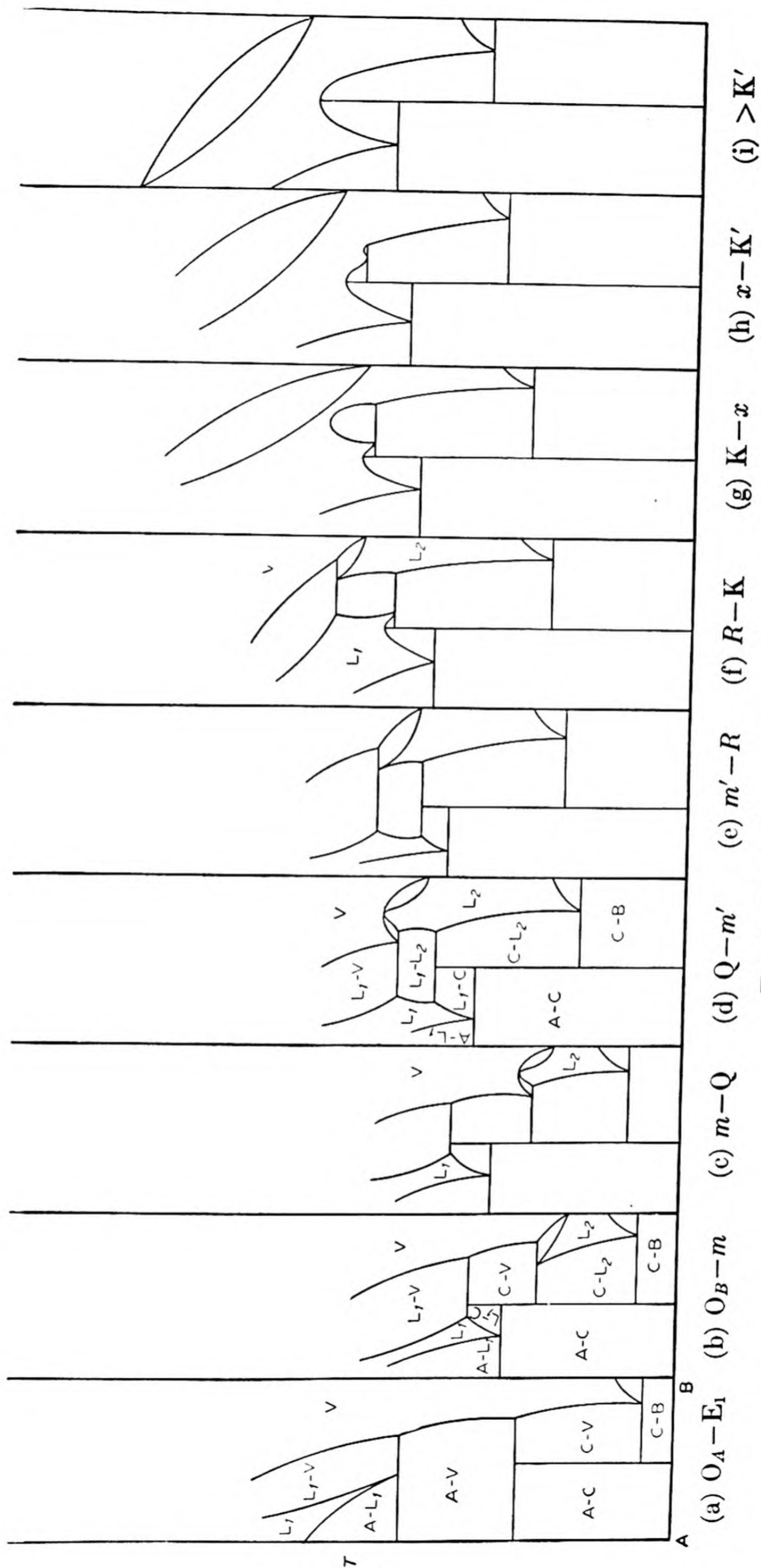


FIG. 8-17. Isobars of Fig. 8-15.

identical while in equilibrium with L_1 . Beyond this point, in respect to P and T , the 3-phase equilibrium L_1L_2V no longer exists, since there is no longer any distinction between V and L_2 , which may now be called the Fluid (Fl) phase, as contrasted to L_1 , a liquid. Hence the critical solution curve $L_1 = L_2$, originating at the lower consolute point K_1 , now becomes continuous with the critical curve $L = V$, or better $L_1 = \text{Fl}$, originating at K_A . Fig. 8-18 therefore shows a single curve, dashed, running from K_1 to

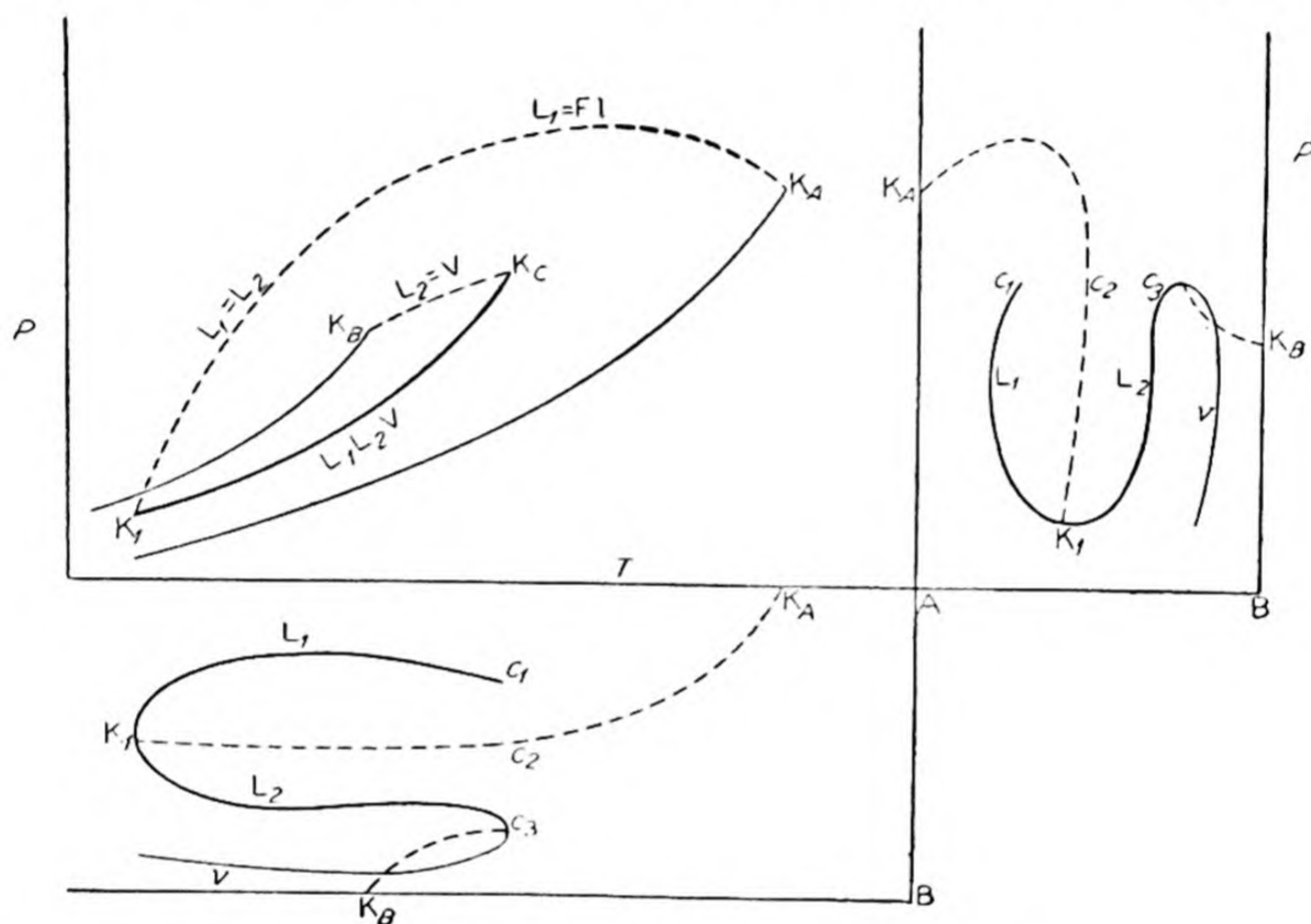


FIG. 8-18. System with critical end-point.

K_A ; the portion near K_1 is labeled " $L_1 = L_2$," as a "consolute curve," and that near K_A , " $L_1 = \text{Fl}$," as a "critical" curve in the usual sense, but it is immaterial where the change in terminology is started, since L_2 and Fl are perfectly continuous and a single phase.

If, therefore, the 3-phase system L_1L_2V is heated at constant volume, the P and T rise according to the curve K_1K_c , while the compositions of the phases vary as shown in the P/c and T/c projections. If the composition lies between c_1 and c_3 , and if the volume (or over-all density) is such as to have all three phases present when the point K_c is reached, then there occurs the special critical point $L_2 = V$, with L_1 present. If the composition lies between c_2 and c_3 , the two phases left at K_c (L_1 and Fl) undergo no further critical phenomenon, whatever the density; the liquid merely evaporates to leave Fl . Between c_1 and c_2 , the phases L_1 and Fl may undergo, with suitable adjustment of density, a second critical phenomenon ($L_1 = \text{Fl}$) on the curve c_2K_A .

If the concentration of B in the complex is $> c_3$, only the usual $L_2 = V$

critical phenomenon can occur on the curve $K_B c_3$. If the concentration of B is $< c_1$, again the only possibility is the usual critical phenomenon $L_1 = V$ on the upper part of the curve $c_2 K_A$.^{20a}

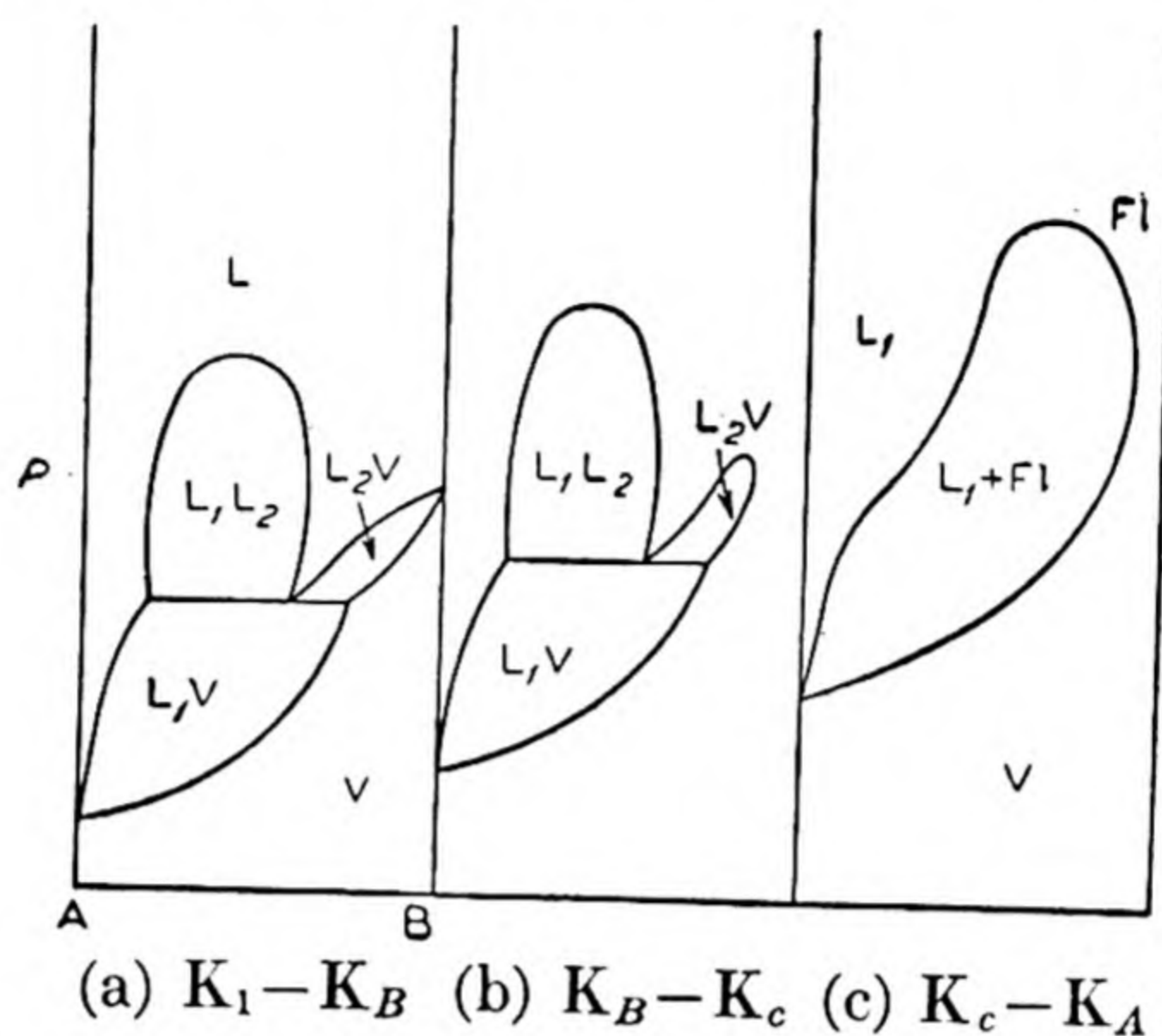


FIG. 8-19. Isotherms of Fig. 8-18.

The relations vary only quantitatively if other relative values for the points K_A , K_c , and K_B are taken, the principles and qualitative relations remaining the same. Some cross-sections of Fig. 8-18 are shown in Figs. 8-19 and 8-20.

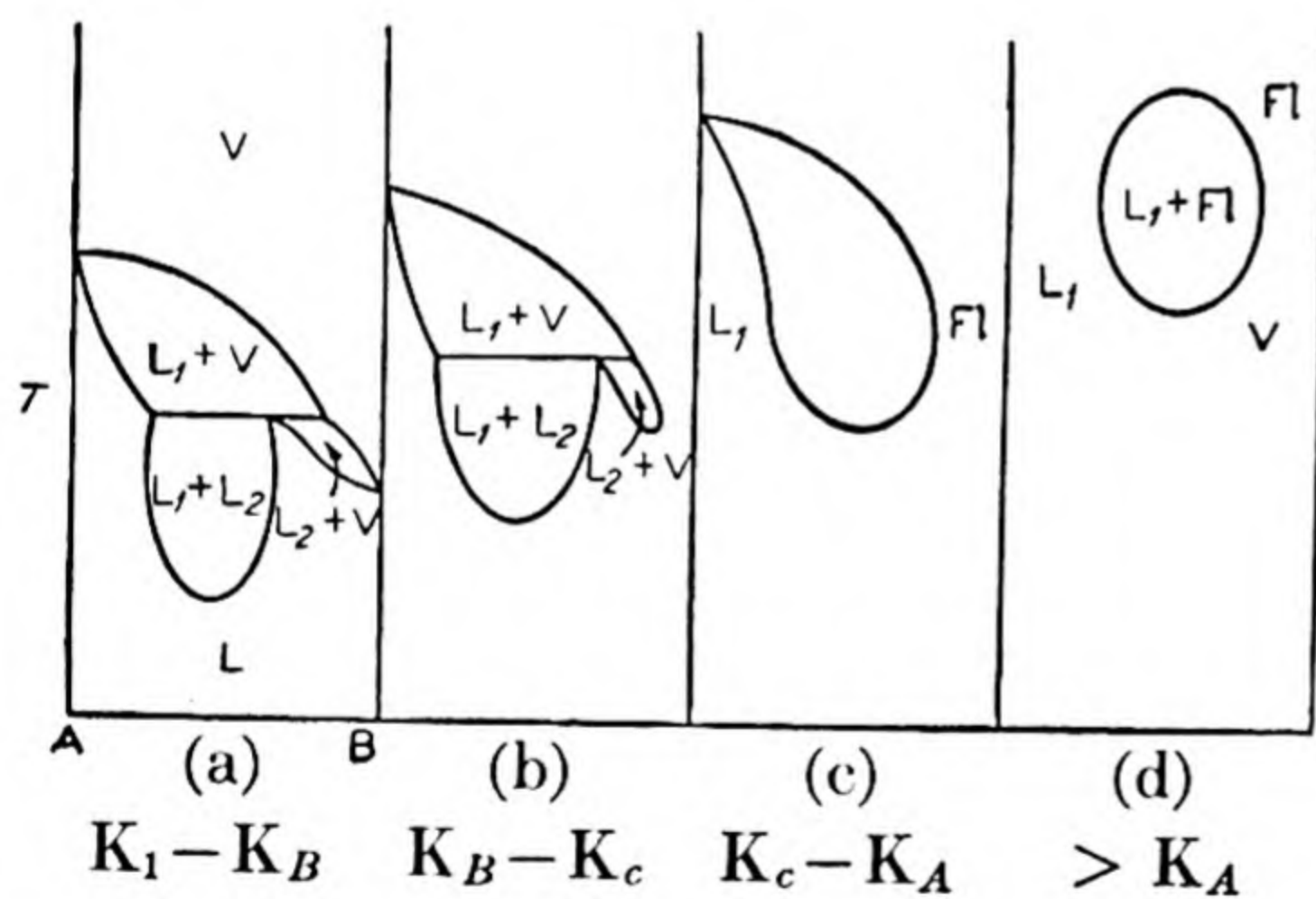


FIG. 8-20. Isobars of Fig. 8-18.

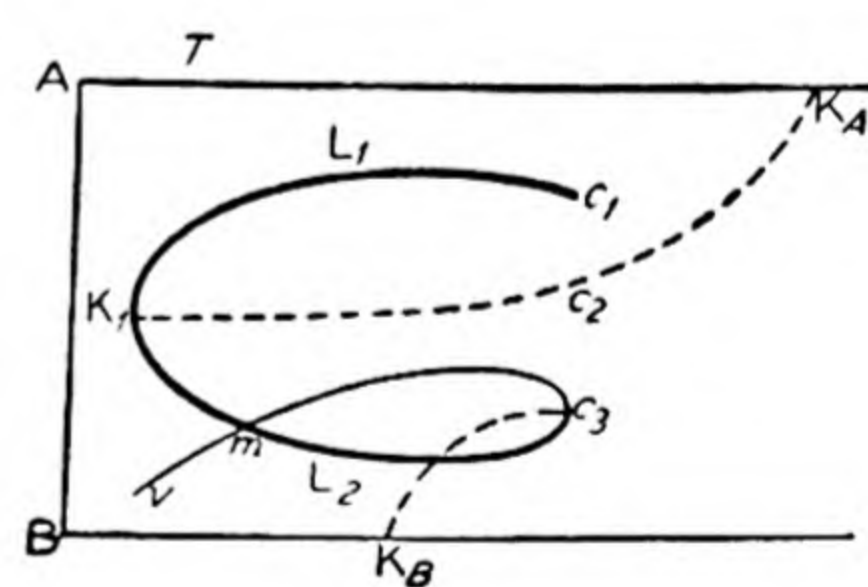


FIG. 8-21. Variation of Fig. 8-18.

In the system propyl alcohol (A)–ethane (B), the P/T projection differs from that of Fig. 8-18 only in that K_1 lies somewhere between K_B and K_c , in respect to both T and P .²¹ The same is true of the system p -dichlorobenzene (A)–ethylene (B).⁷ In the system ether–water there is, of course,

^{20a} For the representation of these relations in the $P/T/c$ space model, see Büchner (Ref. P), II-2, p. 111, and Vogel (Ref. V), p. 158.

²¹ J. P. Kuenen and W. G. Robson, *Z. phys. Chem.*, **28**, 342 (1899).

no lower critical solution point, and K_c is at 205° and 52 atm, with 10% water.^{21, 22} In Fig. 8-18, moreover, the relation of the vapor to the conjugate liquids in respect to composition has been assumed to be always that of Type I, Fig. 4-5(a). Fig. 8-21 shows the T/c projection for a system in which, at the singular point m , similar to that in Fig. 4-7(b), the vapor composition comes to lie between the two liquids, as in the system ether-water,²³ in approaching the critical end-point K_c .

Finally, we may mention that isobaric or isothermal changes at the critical region of these systems may involve what have been called "double retrograde condensation" phenomena, such as the change $V \rightarrow L_1 + L_2 + V$ upon isothermal expansion, etc.²⁴

²² I. C. T., III-382.

²³ F. E. C. Scheffer, *Z. phys. Chem.*, **84**, 728 (1913).

²⁴ J. van der Waals, *Arch. néerland. sci.*, [II], **15**, 126 (1910); see also D. L. Katz and F. Kurata, *Ind. Eng. Chem.*, **32**, 817 (1940).

Chapter IX Condensed Binary Diagrams and Their Determination

Preliminary; Characteristics of the Diagrams

The majority of familiar and important phase diagrams are those of the "condensed system," determined in open air without regard to the composition of the vapor phase, or in closed apparatus, with vapor present but without regard either to the pressure or to the composition of the vapor at all. All the equilibria shown in these diagrams involve the vapor phase, so that "high pressure phenomena" are not shown, but the vapor is not plotted and is not even counted as one of the phases in the following discussion. Certain general relations and properties of condensed binary diagrams will here be summarized; they apply in the construction of the diagram from the data determined according to the methods to be discussed.

The condensed diagram represents the T/c relations of condensed phases under the pressure of the system; the temperature will be called the vertical axis. The diagram consists of two kinds of areas or fields. A homogeneous area, with no tie-lines, represents a single phase in "condensed" bivariant equilibrium. If the phase is a pure solid, the homogeneous "area" is a vertical line or an infinitesimally narrow area. A heterogeneous area represents two coexisting phases in "condensed" univariant equilibrium and is filled with isothermal tie-lines ending at the limits of homogeneous areas. The two kinds of fields are separated, in respect to changes in composition and temperature, by curves, all of which may be called solubility curves, representing either phase transitions or outlines of miscibility gaps.

The two curves of a phase transition may have smooth maxima or minima, and these are points at which the two phases involved have the same composition, such as a solid solution of minimum melting point or a congruently melting compound. (We here ignore as negligible the difference between T_m and M in the condensed diagram of a system with congruently melting binary compound; cf. Fig. 7-34 and the discussion of it.) One of the phases involved may therefore be pure. Through a smooth maximum or minimum of a transition curve, the system appears to pass, with change of temperature, directly from one homogeneous area to another, according to the condensed diagram, but it passes, actually, through a 2-phase equilibrium which is a condensed invariant because of the equality of composition

of the two phases. These phase transition curves may also have breaks in them, but never, if liquid is involved, at a maximum, in a true binary system. Each break occurs at a 3-phase tie-line or at a condensed invariant equilibrium. If the break is at a temperature minimum, it is a eutectic (or a eutectoid) and otherwise transitional or peritectic (or peritectoid).

The curves of a miscibility gap, representing conjugate solutions, liquid or solid, are terminated, with respect to T , either by a 3-phase tie-line (a condensed invariant equilibrium) or by a critical solution point which is a smooth maximum or minimum of the MG and also a condensed invariant by restriction. The latter is simply a point on a "closed" solubility curve (binodal curve), and the system may pass through directly, as through any solubility curve, between a homogeneous and a heterogeneous area.

A 3-phase tie-line (or condensed invariant equilibrium), whether it terminates a phase transition equilibrium or a miscibility gap, has one heterogeneous area on one side and two on the other, the latter two being divided by the tip of a homogeneous area or by a line representing the composition of a pure compound. If a complex lies in the tip of this homogeneous area, or if we are dealing with the pure compound, and if T is changed to cross the 3-phase tie-line, the system appears to pass directly from a homogeneous area to a 2-phase area, but it first suffers a "condensed" invariant 3-phase reaction. Thus if the eutectic liquid is cooled, the temperature is constant while the reaction $L \rightarrow S_A + S_B + \text{cals.}$ proceeds to completion.

Since the variables of the condensed diagram are T and c , the methods of determination may be classified as either isothermal or isoplethal.

A. Isothermal Methods

These involve the determination of the composition of the boundaries of the areas, and hence of solubilities, at known T . For either the solid-liquid or the liquid-liquid solubility curves, this may be accomplished by the separation of the phases at equilibrium (usually easy for the separation of L from S , or L_1 from L_2) followed by analysis (chemical or physical). The isolation of S from L is often difficult even by centrifuging, especially if one component is volatile or if the solid is very finely divided, mechanically retaining liquid.

The composition of the saturated solution may be obtained without separation from the solid, by plotting, isothermally, the value of any property of the liquid as a function of the total composition of the complex or system. As solid A is added to liquid B , any property of the unsaturated liquid will vary smoothly with respect to the total composition as long as the liquid remains unsaturated. A break in the plot may then be used to find the composition of the saturated liquid or the solubility of A in liquid

B. For this purpose any property at all of the liquid could theoretically be used, but the most convenient property would depend on the specific nature of the system in question: density, refractive index, conductivity, etc. Such procedure, of course, does not allow us in general to identify the solid phase, but it can be used to plot the liquidus, if the experiment is made at a sufficient number of temperatures.¹

Special isothermal methods are possible for liquid-liquid solubilities, eliminating the necessity of separation and analysis. One is that of titration of one liquid with the other, since a second layer, visible as a turbidity, appears when the boundary of the *MG* is reached;² if the titration is reversed, the conjugate point, or the other boundary of the *MG*, may similarly be determined. The second is the method of Hill (1923)³ in which two complexes of different total composition are made up, at the same temperature, and the volumes of the conjugate liquid layers at equilibrium are measured. The compositions of the conjugate liquids in the first complex are the same as those in the second. Hence it is possible to calculate their compositions (and their densities) from their measured volumes and the original weights of the components taken. The principle is also applicable⁴ to the determination of the liquid-vapor equilibrium compositions of a binary system at constant *T* and *P* and is essentially the same as that used in determining the orthobaric densities of *L* and *V* approaching the critical point for a one-component system.

The accuracy of these isothermal methods for the liquid-liquid equilibrium falls off as a critical solution point is approached, when the derivative dc/dT approaches infinity.

For relations between solid phases, such as the mutual solubility or the interactions below the melting point curve, in systems consisting of metals or of salts, for example, these direct isothermal methods are not applicable. In such cases the system may be made to come to equilibrium at a specified temperature and then quenched. If the equilibrium is frozen, the phases are then studied for identification or analysis by physical methods, such as microscopy or X-ray examination. In some cases such information may be obtained from a study of the isothermal solubility relations of a ternary system containing a liquid solvent as third component. If this liquid forms no compounds with the two solids, the isotherm yields the required information on the binary system. This will be discussed further in Chapter XIII,

¹ The use of refractive index in this connection was illustrated in papers by J. E. Rutzler and R. G. Bauman, Spring Meeting of the American Chemical Society, Chicago, 1948.

² W. Herz., *Ber.*, **31**, 2669 (1898).

³ A. E. Hill, *J. Am. Chem. Soc.*, **45**, 1143 (1923).

⁴ G. Calingaert and L. B. Hitchcock, *ibid.*, **49**, 750 (1927).

but two applications have already been mentioned, under Figs. 6-3(a) and 6-5(d).

B. Isoplethal or Synthetic Methods

These involve the measurement of the temperature of phase transition or of the curve of a miscibility gap, upon complexes of known composition.

1. Visual Observation

In this method one observes the temperature of appearance or disappearance of a particular phase. For the liquid-liquid *MG*, this is known as Alexejff's method;⁵ it may be applied with either falling or rising temperature, using sealed samples, when it has the advantage of permitting repeated observation on the same sample. The accuracy is low along the sides of the *MG*, when the derivative dT/dc approaches infinity, but it is more effective in fixing the temperature of the curve near consolute points. The consolute concentration may then be obtained by plotting the analytical (isothermal) data according to the law of Cailletet and Mathias, as mentioned in Chapter IV.

The visual method is much used also for the solid-liquid transition, particularly in systems involving organic substances. Refinements make use of microscopic observation, with hot-stage technique, polarographic microscopes, etc. In general the liquidus is much more easily determined than the solidus; the liquidus is the temperature of the first appearance of solid on cooling or of the disappearance of the last trace of solid on heating. Whereas supercooling or metastability is rarely a serious problem in the liquid-liquid determinations, it is here frequently a serious limitation on the method. The determination of the solidus by this method requires the observation of the disappearance of the last trace of liquid on cooling, or the first appearance of liquid on heating, in either case an observation which may be of questionable dependability. (See, for example, the discussion on purification by recrystallization, in Chapter V, section A.) Much work is nevertheless done, with the so-called **thaw-melt** method of Rheinboldt,⁶ using very small samples. The "thaw-point" is then taken as the solidus, involving the assumption that the solids are in equilibrium when they reach the solidus and involving the difficulty of observation just mentioned; and the point of complete melting is taken as the liquidus. The solidus thus observed will always appear to rise toward the melting points of the pure components, near the sides of the diagram. The method therefore can, in general, set a limit to the degree of solid solubility of the com-

⁵ M. W. Alexejff, *Bull. Soc. Chim.*, **38**, 145 (1882).

⁶ H. Rheinboldt, *J. prakt. Chem.*, **111**, 242 (1925).

ponents, but it is often inconclusive as to whether the components crystallize in the pure state or with some degree of solid solution.

2. Thermal Analysis

In this method⁷ the sample is allowed to cool (or to warm up) under some set of regulated conditions, such as a constant surrounding temperature for the transfer of heat, a constant temperature differential with respect to the surroundings, a constant rate of temperature change, or a constant rate of heat transfer, etc. The temperature of the sample is then plotted against time, and if the experiment is repeated on a series of samples of known composition, from pure A to pure B, the corresponding breaks and halts in the cooling or heating curve may be used to construct the phase diagram. Whatever the phase diagram, the successive equilibrium states traversed by a particular complex as its temperature changes, are distinguished with respect to the number and nature of the phases involved, each change occurring either at a curve or at a horizontal (a condensed invariant) line of the diagram. Every such change is, in general, accompanied by a break or an abrupt change in the rate of cooling or heating, and every invariant state by a halt or a period of constant temperature. If the changes in heat content are simultaneously measured, the information is fuller and furnishes corroboration for the deductions based on the T/t (temperature-time) curve. In practice we may also employ a plot of the rate of change of T with respect to time, or better, of the derivative dt/dT , against T , to fix the temperature of the initiation or completion of a phase reaction or transition; the value of the derivative dt/dT is theoretically infinite at an invariant temperature, for example.

In the schematic cooling curves here shown, complete equilibrium is assumed to prevail at every point; they represent therefore ideal or reference curves to which the actual, observed behavior merely approximates, because of the lack of equilibrium in various respects: supercooling for phase transitions, lack of internal equilibrium in the case of solid solutions, and unequal temperature distribution in the sample.

Fig. 9-1 shows the schematic cooling curve of a pure substance with enantiotropic polymorphism (S_α the lower, S_β the higher temperature form). The slopes of the univariant sections (here the one-phase sections) depend on the experimental conditions and on the thermal properties of the substance. The temperature of the first halt is the freezing point, and its length (time duration) depends on the apparatus, the heat of fusion, and the quantity of material. Supercooling and imperfect temperature distribution

⁷ Apparently first suggested and discussed by G. Tammann, *Z. anorg. Chem.*, **37**, 303 (1903); **45**, 24 (1905); **47**, 289 (1905).

cause the curve to have the appearance indicated by the dotted lines at the freezing point. The second halt occurs at the enantiotropic transition temperature; its length now depends on the latent heat involved, but even if its length is practically zero, it will mark a break in the curve accompanied by some slight change in slope because the two forms S_α and S_β will differ in heat capacity.

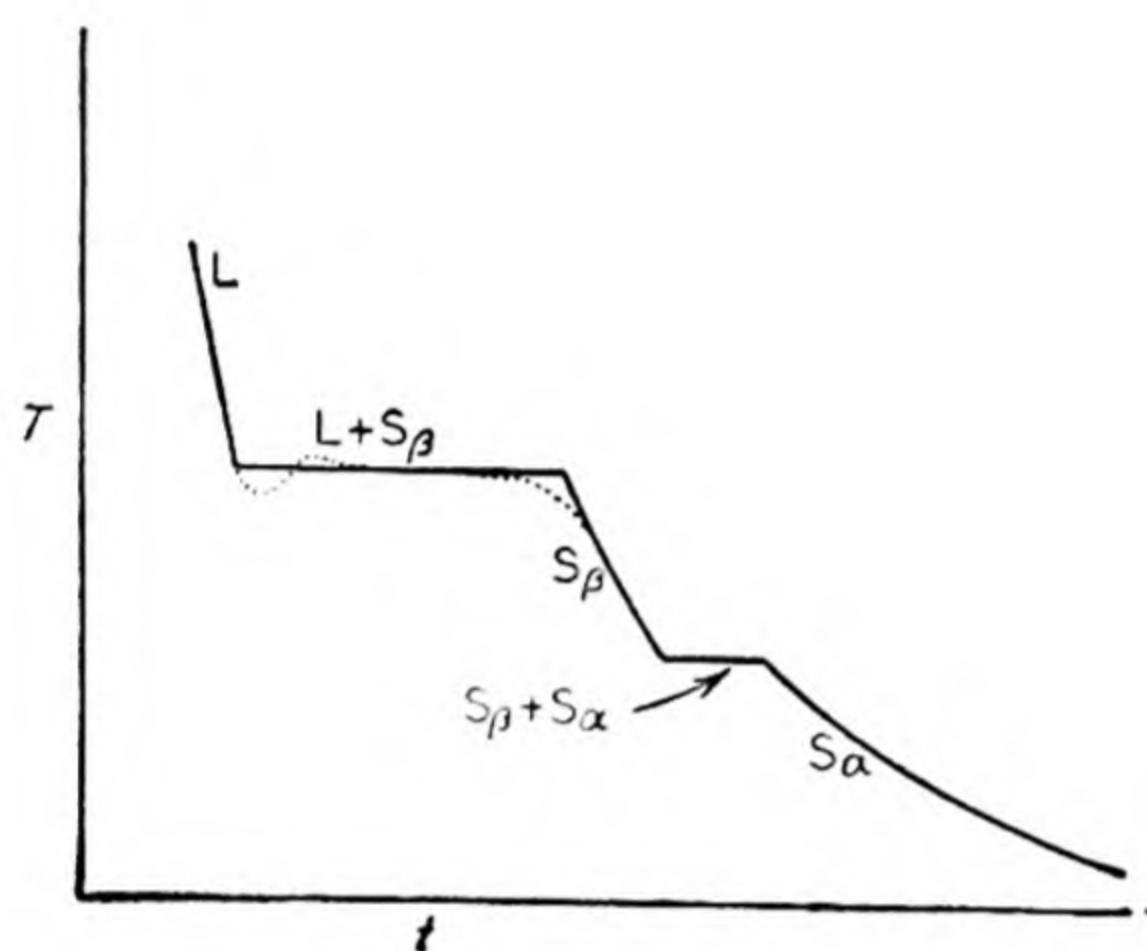


FIG. 9-1. Cooling curve of pure substance.

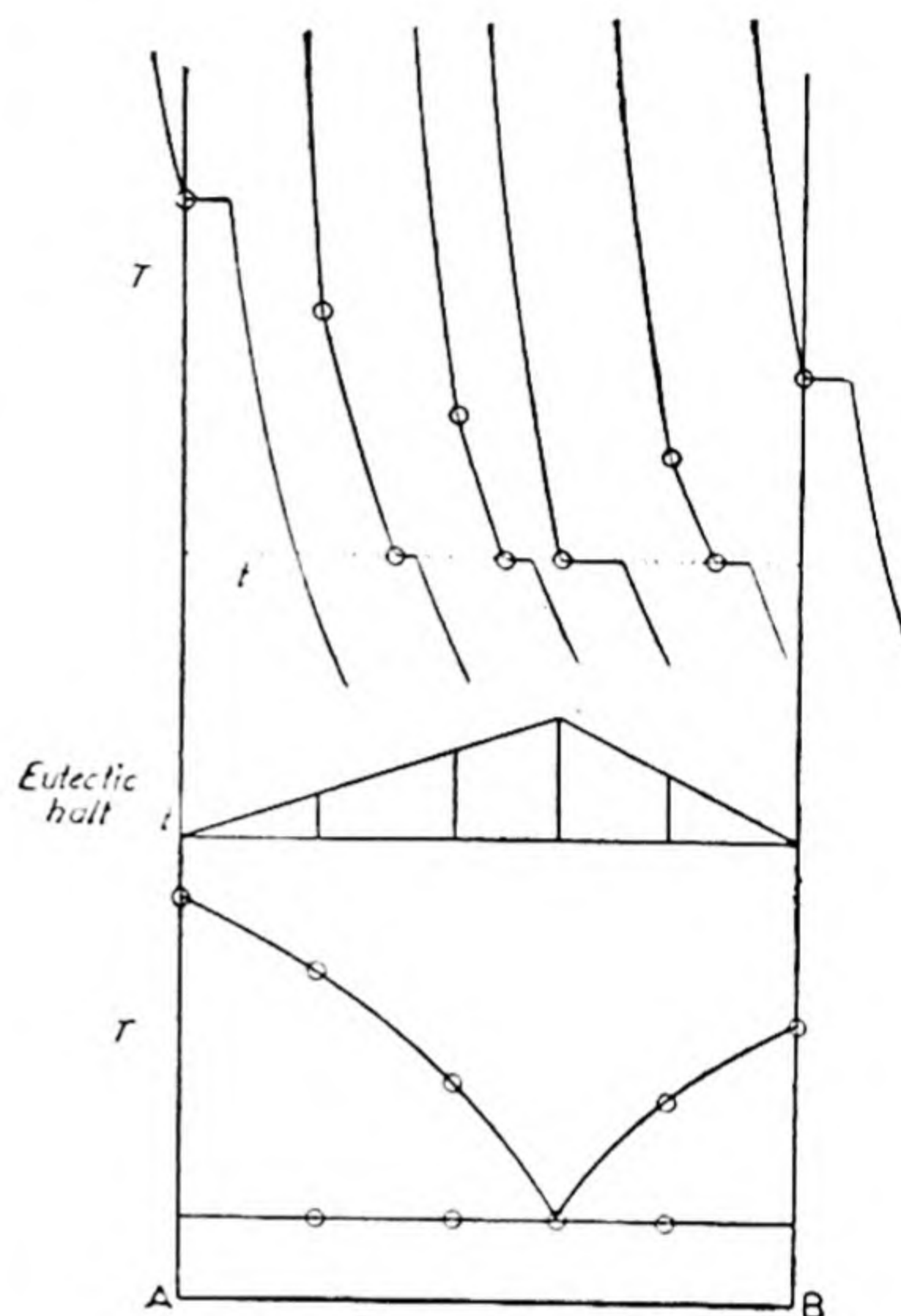


FIG. 9-2. Simple eutectic system.

If a binary liquid, in a simple eutectic system involving pure solids, is cooled, the rate of cooling decreases abruptly when a freezing point curve is reached because of the exothermal crystallization of a solid; the temperature of this break varies with the composition of the sample. When the eutectic temperature is reached, the temperature is constant; the duration of the halt, for constant amount of sample, depends upon the quantity of eutectic liquid to be solidified, so that it is a maximum if the sample has the eutectic composition. The cooling curves for six samples are plotted, T against t , in the first part of Fig. 9-2; the length of the eutectic halt against composition, t against c , in the second part; and the phase diagram, T/c , in the third part. The first break is said to mark the start of the primary crystallization, in this case that of pure A or pure B. During the period of constant T (eutectic halt), there occurs the crystallization of a eutectic mixture of A and B, in the proportions of the eutectic liquid. This results in a mixture which is physically heterogeneous in two senses: primary crystals of A or B, and a eutectic mixture of A and B, which may appear as a matrix embedding the primary crystals. The eutectic mixture, in the case of metals, is sometimes granular and sometimes lamellar in structure.

If the system is eutectic with limited solid solution, the eutectic halt

occurs only for solutions in a limited range of composition. Outside this range the liquid disappears on cooling before this temperature is reached,

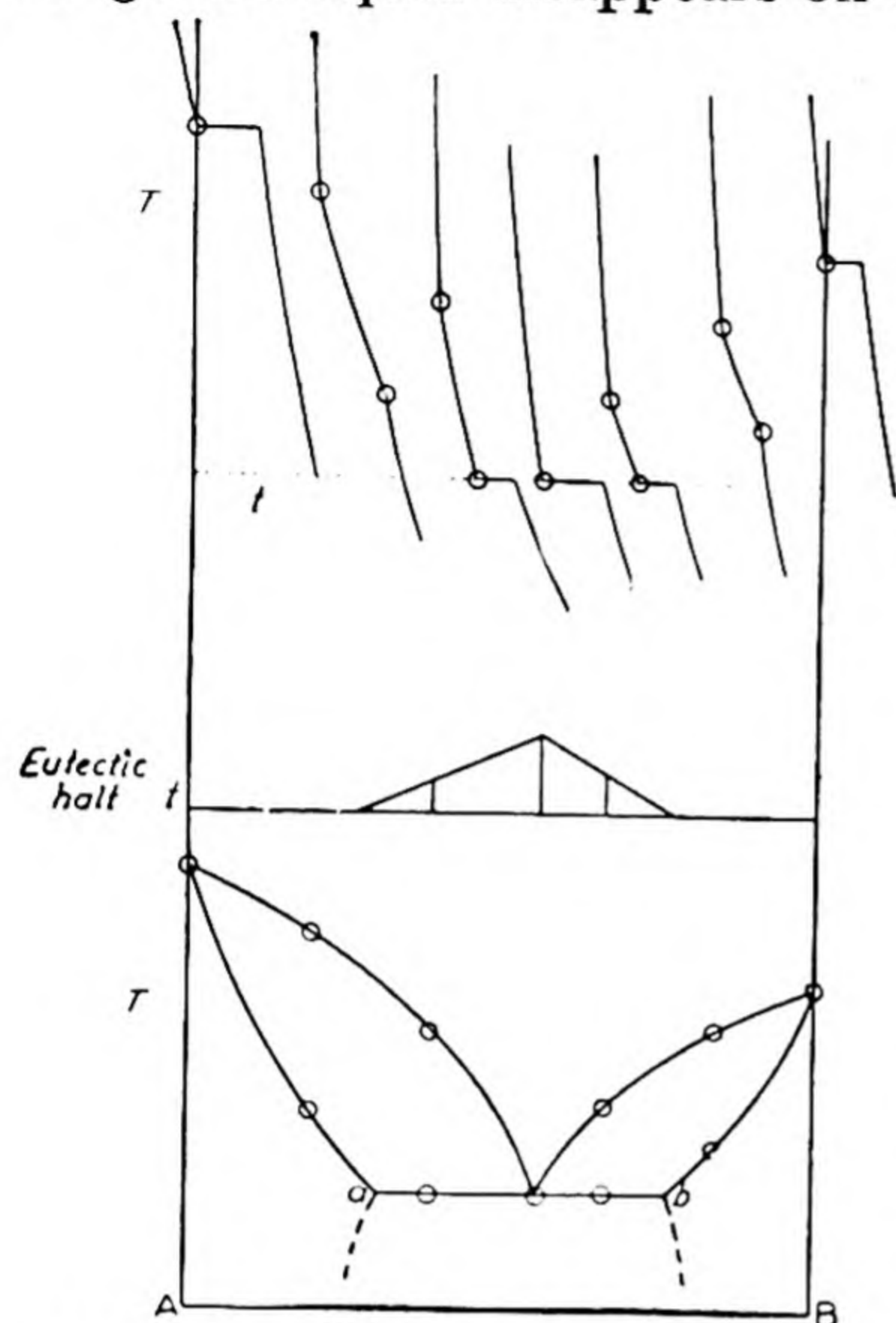


FIG. 9-3. Eutectic system with solid solution.

the reaction $S_1 + L \rightarrow S_2 + \text{cals.}$, is a maximum for the composition c_2 and vanishes at c_1 and c_3 .

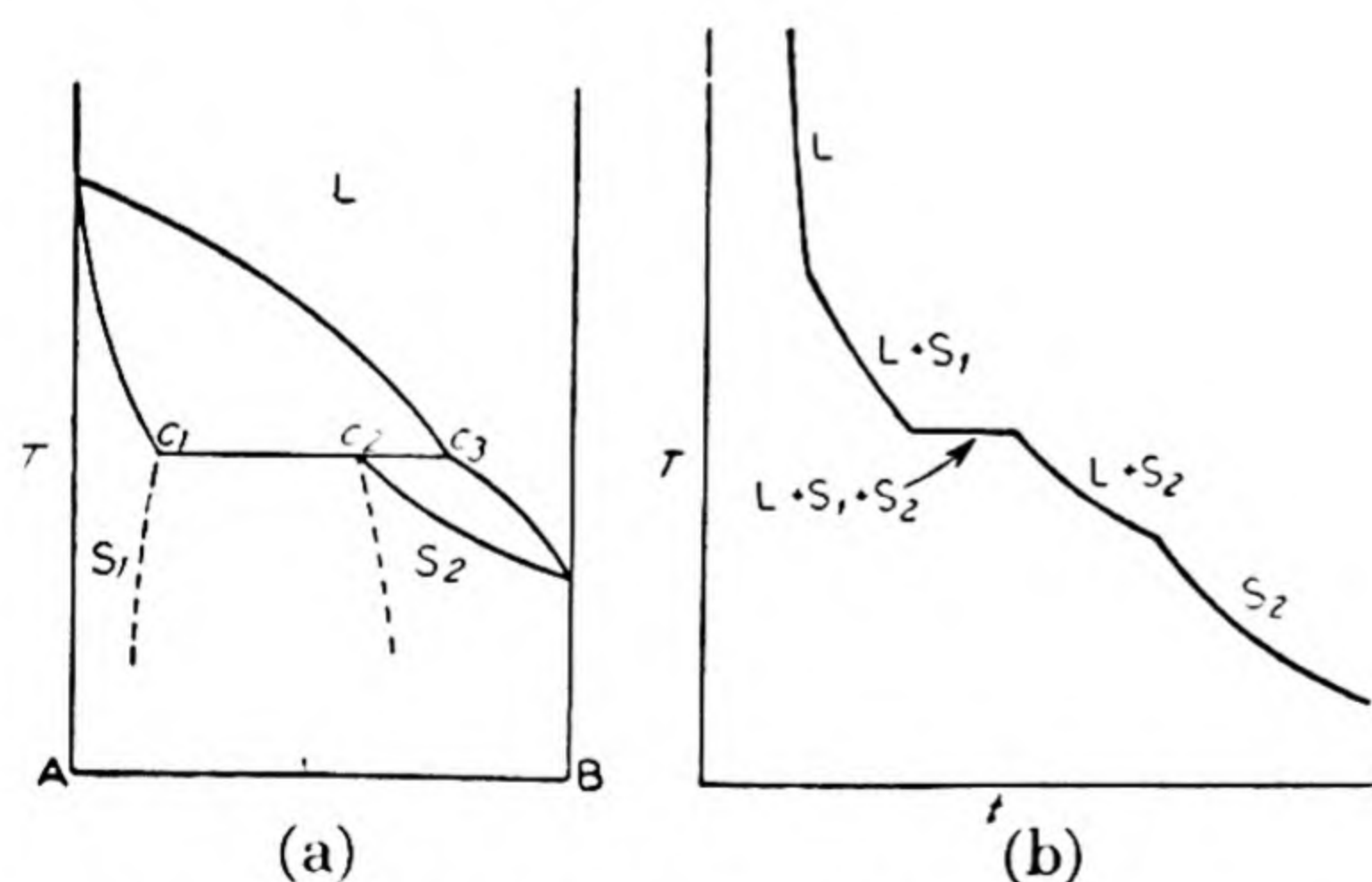
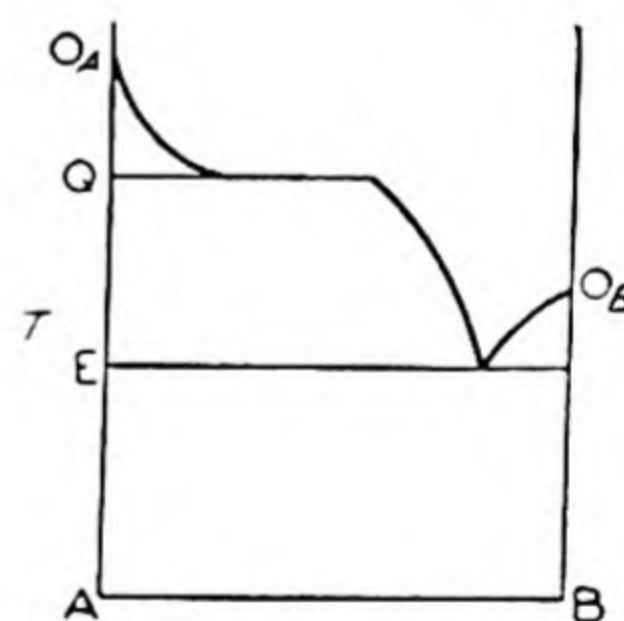


FIG. 9-4. Solid solution with peritectic.

FIG. 9-5. System with liquid MG .



The dotted portions of the diagrams of Figs. 9-3 and 9-4, representing the outline of the MG below the melting point curves, will not generally show effects on the cooling curve.

For a system with continuous solid solution, both the liquidus and the

but the change from the system $L + S$ to S is marked by a second break in the cooling curve, defining the solidus (Fig. 9-3). If the points a and b , presumably the conjugate solid solutions at the eutectic, are close to pure A and pure B respectively, then again, as in the visual (thaw-melt) method (and for the same reasons), we can only set limits to the mutual solubility of the solids but cannot establish very definitely whether or not the solids are pure.

If the system is peritectic with solid solution, there will be a range of composition, between c_2 and c_3 of Fig. 9-4(a), in which a cooling curve, always assumed to involve equilibrium relations, will show four breaks, as in Fig. 9-4(b). The length of the invariant halt, for the phases L , S_1 and S_2 , depending on

solidus will be marked by breaks, but there will be no invariant halt unless there is a maximum or a minimum in the melting point curve. If the composition is that of such a maximum or minimum, the behavior is like that of a pure substance in the cooling curve at any given pressure.

In a system like that of Fig. 8-6, with a 2-liquid area on a freezing point curve, thermal analysis does not detect the outline of the MG , but there will be breaks along the freezing point curves ($O_A l_1$, $l_2 c$, $c O_B$) and invariant halts at Q for compositions between A and l_2 , and at the eutectic E for the whole system. The diagram for such an alloy system, for example, as deduced from thermal analysis, would then appear as in Fig. 9-5.

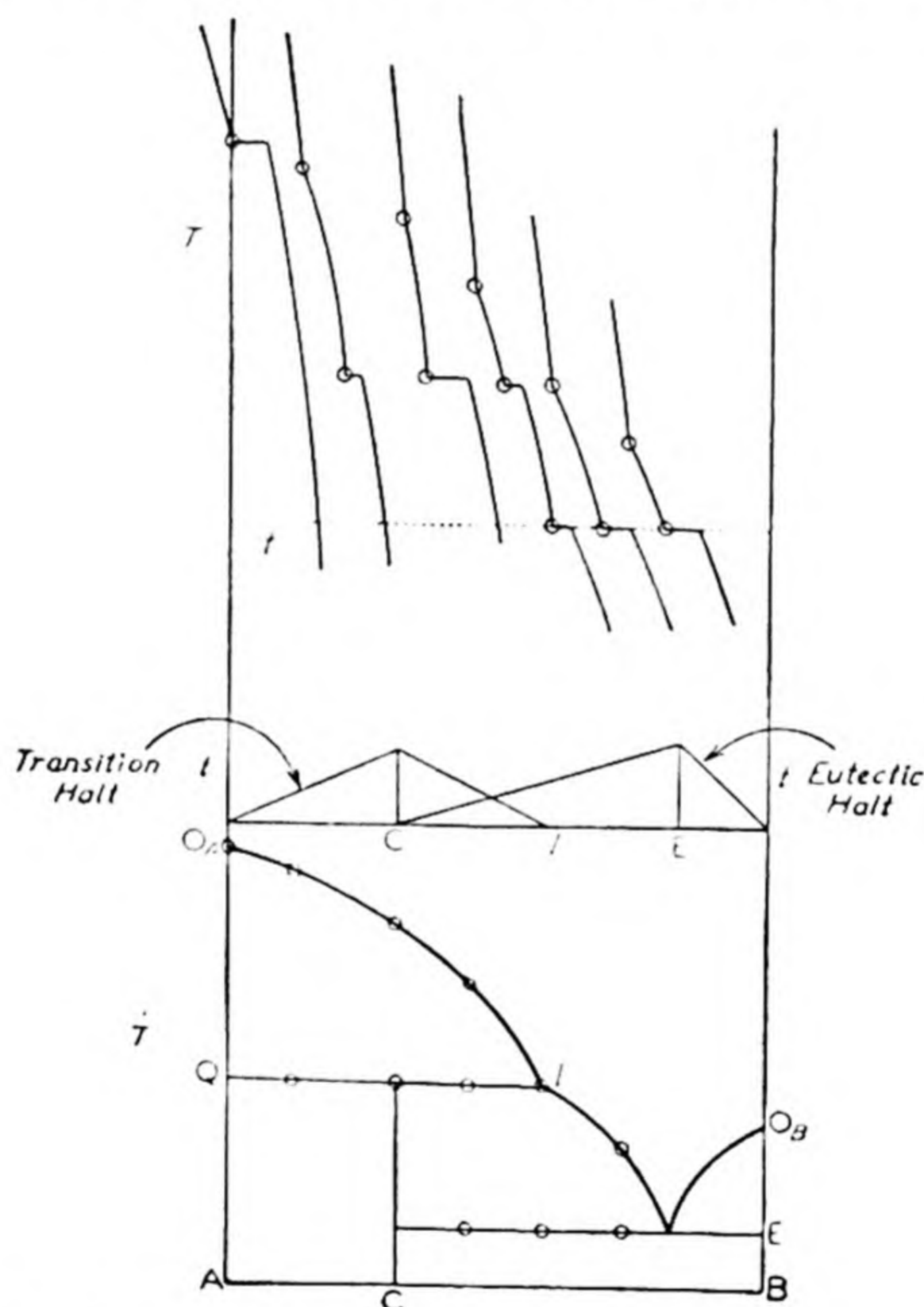


FIG. 9-6. Incongruently melting compound.

If the system involves a compound with congruent melting point, the latter acts as a pure substance and thermal analysis leads to a diagram like two of the systems of Fig. 9-2 set side by side, with the composition of the compound given by the maximum in the freezing point curve between two eutectics. For an incongruently melting compound, there will be two constant temperature halts: the transition point Q , shown by compositions between A and l (Fig. 9-6), with a maximum duration for the composition C of the compound itself, during the phase reaction $l + A \rightarrow C + \text{cals.}$, and the eutectic E , shown by compositions between C and B , with a maximum

duration for the composition E as usual. The composition of the compound, therefore, is not given by the freezing point curve, which has no maximum in this case; but it is given as the composition of maximum transition halt. The freezing point curve itself is plotted as usual from the temperatures of initial crystallization.

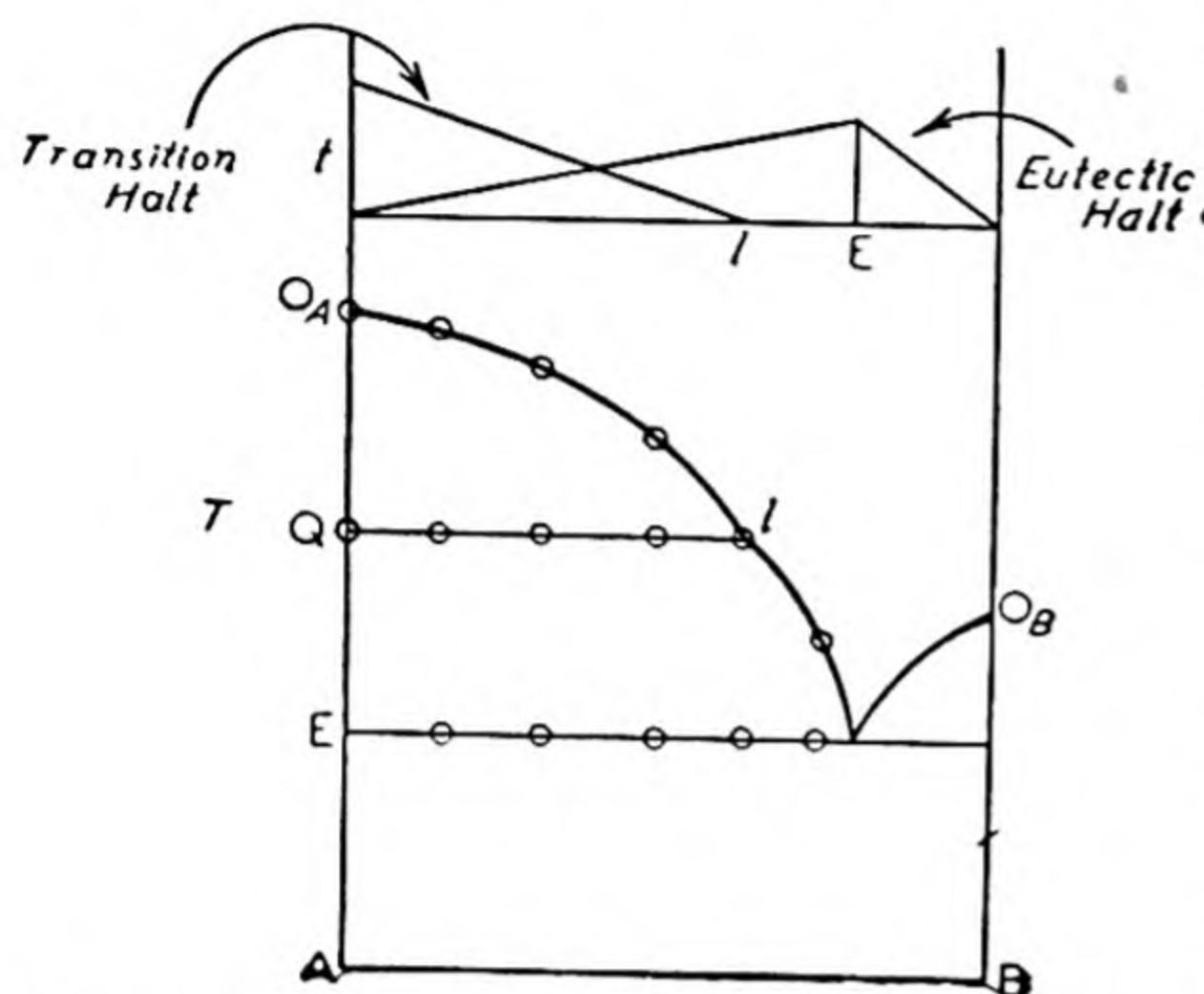


FIG. 9-7. Polymorphism of solid A.

For compositions between A and *l* there are two invariant halts, that for polymorphic transition at Q, and the eutectic E; but the transition halt is now a maximum at pure A, and the eutectic halt does not disappear (theoretically) until pure A is reached.

3. Dilatometry

The technique of thermal analysis, through cooling or heating curves, even if perfectly standardized in respect to thermal problems, has the inherent difficulty of the problem of the internal equilibrium of the sample itself. It is a moving or dynamic technique, and the experimenter cannot wait, with the system at constant *P* and *T*, to prove the establishment of equilibrium, homogeneous or heterogeneous. Despite subdivision of the sample, stirring, seeding, etc., the ultimate test of time, for the establishment of equilibrium, cannot be applied since time itself is a working variable. In some cases the reversal of the direction of the experiment, in respect to temperature change, may be a satisfactory substitute.

In dilatometry time is not a variable, but the volume of the sample of known composition is plotted against the temperature at constant pressure. It is hence possible, at least theoretically, to take sufficient time to maintain equilibrium all along. The principles, however, for deducing the phase diagram from the plot of volume against *T*, or of $d(\text{vol.})/dT$ against *T*, are the same as in thermal analysis. This derivative changes abruptly as the sample passes from one equilibrium state to another, with a change in the number and nature of the phases involved. Hence the various curves and divisions of the (condensed) diagram may be plotted from dilatometric

measurements on synthetic samples of known composition, undergoing changes of T in the open air, or at more or less constant pressure. The derivative is usually small for the system in the state of a single phase; its absolute value, whether positive or negative, increases abruptly as a 2-phase region is entered and becomes infinite during isobaric invariance. The method is therefore useful for the determination, for example, of a transition point, whether unary or binary. Many properties other than density may also be used in the same general manner for detecting the appearance or disappearance of phases as the temperature of the sample is changed. As an example we may mention the electrical conductivity, used in the study of the liquid MG of the system ammonia-sodium, with an upper consolute temperature, at atmospheric pressure, of -41.6° at 4.15 atom percent of sodium.⁸

For phase relations at high pressure, the sample, at constant T , may be subjected to compression, and the volume or the movement of a piston may be plotted against the pressure. This is the technique used by Bridgman in the study of the high pressure polymorphism of the elements and is also applicable, of course, to binary systems.

4. Calorimetry

If the heat content of the sample of known composition is measured at constant P as $f(T)$, the method is theoretically almost identical with that of dilatometry, being likewise potentially an equilibrium method. The calorimetric method yields not only the phase diagram but also the heats of transition involved. A variation of thermal analysis known as differential thermal analysis, in which one plots not only the temperature T against the time t , but also the difference in T between the sample and a reference substance against either T or t , may also be used to obtain the heats of transition together with the phase diagram.⁹

At this point we may repeat that a phase diagram is by definition an equilibrium diagram, whether stable or metastable; and no refinement of measurement avails anything unless the measurement is that of an equilibrium state. As an interesting example of apparent phase diagrams representing what we may call different degrees of attainment of equilibrium, Fig. 9-8 shows the apparent freez-

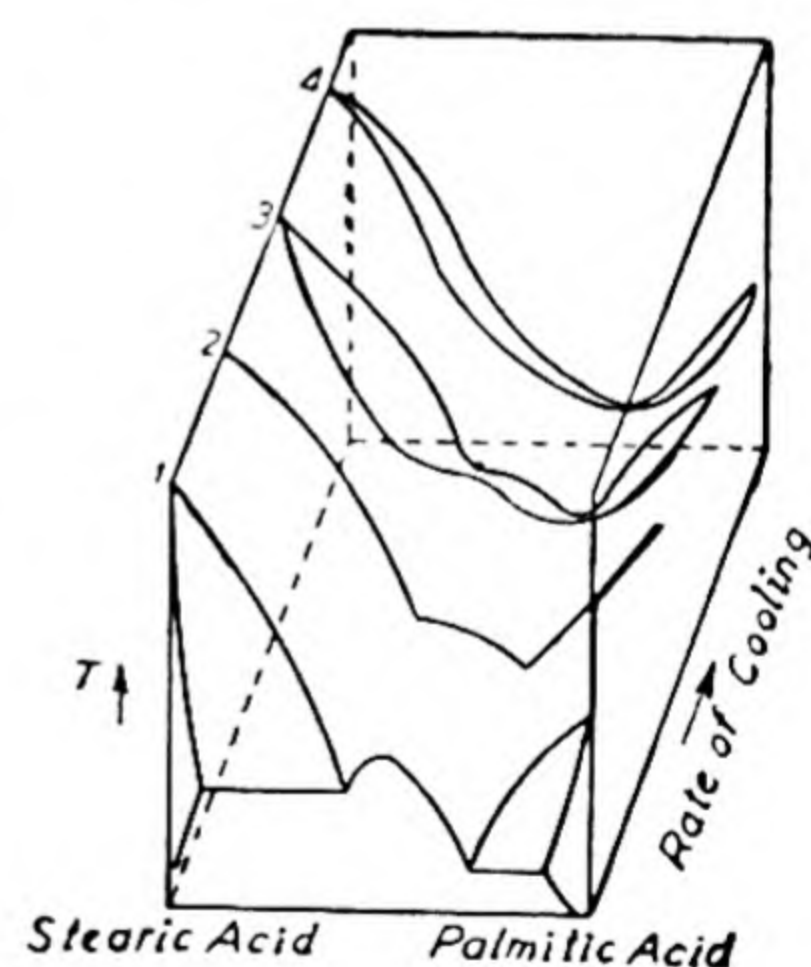


FIG. 9-8. Apparent diagrams and rate of cooling.

⁸ C. A. Kraus and W. W. Lucasse, *J. Am. Chem. Soc.*, **44**, 1949 (1922).

⁹ See, for example, M. J. Vold, *Anal. Chem.*, **21**, 683 (1949).

ing point relations in the system palmitic acid–stearic acid as a function of the rate of cooling.¹⁰

C. Purity Determination

It is possible in some cases to use either cooling curves or heat content curves for the determination of the purity of substances. The interpretation of time-temperature freezing and melting curves for this purpose has been developed most thoroughly by Rossini and his co-workers.¹¹ If a substance is impure, the section L + S of its cooling curve is, in general, no longer horizontal. If the impurities are liquid-soluble but not solid-soluble, the temperature will fall along this section, as the residual liquid becomes increasingly concentrated with respect to the impurities. If the solution is ideal and the solid pure, this temperature will vary linearly — for low concentrations of impurity — with the reciprocal of the fraction melted. If then the cooling curve of a given sample gives such a relation, it is reasonable to infer that the solid is pure, the impurities only liquid-soluble, and the solution ideal; whereupon it is possible to calculate, from the observed curve and its slope, and the known heat of fusion, not only the mole fraction x of total impurity (or impurities) but also the freezing point of the pure substance. For the conditions assumed, equation V-1 may be used to express the lowering of the freezing point of solid A, for small values of x_B , the mole fraction of B in the liquid:

$$\Delta T = T_0 - T = \frac{RT_0^2}{\Delta H} x_B, \quad (1)$$

in which T_0 and ΔH refer to pure solid A. Now if x is the mole fraction of B in the original sample, and if n is the fraction of the sample melted (presumably in terms of moles), this expression becomes, still always for small x ,

$$T = T_0 - \frac{xRT_0^2}{\Delta H} \left(\frac{1}{n} \right). \quad (2)$$

Hence if the values of T fall on a straight line when plotted against $1/n$, the reciprocal of the fraction melted, the intercept gives T_0 and the slope then gives x , if ΔH is known.¹²

¹⁰ From G. B. Ravich and V. A. Volnova, *Acta Physicochimica*, U.R.S.S., **17**, 323 (1942). Curve 1 represents their own findings; curve 2, those of L. E. O. DeVisser, *Rec. Trav. Chim. Pays-Bas*, **17**, 182 (1898); curve 3, those of E. Carlifanti and M. Levi-Malvano, *Gazz. Chim. Ital.*, **39**, 353 (1909); and curve 4, those of N. N. Efremov, *Bull. Ural Polytechn. Inst. (Russ.)*, **6**, 155 (1927).

¹¹ W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, **32**, 197 (1944), RP 1585; A. R. Glasgow, A. J. Streiff and F. D. Rossini, *ibid.*, **35**, 355 (1945), RP 1676; A. R. Glasgow, N. C. Krouskop, J. Beadle, G. D. Axilrod and F. D. Rossini, *Anal. Chem.*, **20**, 410 (1948).

¹² See, for example, K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, **63**, 2419 (1941).

In the calorimetric method,¹³ a similar calculation, also applicable¹⁴ only with the same limitations, is made on the basis of the "pre-melting" (Fig. 9-9). The full curves of Fig. 9-9 show the theoretical behavior of a pure

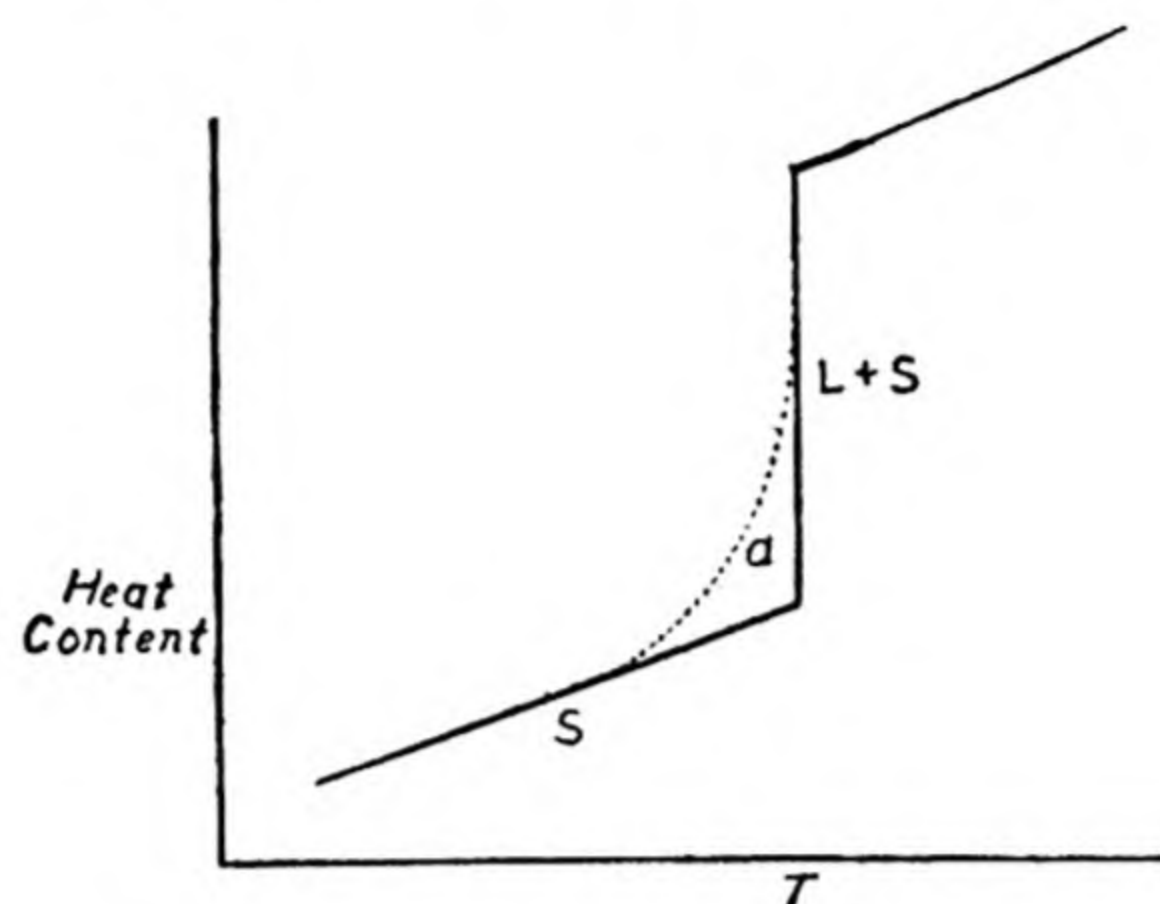


FIG. 9-9. Heating curve.

substance being heated at constant pressure; the dotted curve that of an impure sample. The area *a* is the heat of "pre-melting," and "pre-melting" is simply the term used, in this connection, for what was described as a "range of melting point" for an impure substance under Fig. 5-1(b).

¹³ H. L. Johnston and W. F. Giaque, *J. Am. Chem. Soc.*, **54**, 2610 (1932).

¹⁴ For recent applications, see J. G. Aston and H. L. Fink, *Anal. Chem.*, **19**, 218 (1947), J. G. Aston, M. R. Cines, and H. L. Fink, *J. Am. Chem. Soc.*, **69**, 1532 (1947).

Chapter X Ternary Systems; General Relations

A. Introduction

There are two types of ternary systems. In the **additive** ternary system the compositions of all phases can be expressed additively and in positive terms, in respect to the three components A, B, C, as in systems of three metals. In the **metathetical** or **reciprocal** type the phases have compositions which may be expressed in terms of three of four substances related by the double decomposition $AB + CD \rightleftharpoons AD + CB$. With the restriction that $\Sigma(A + C) = \Sigma(B + D)$ in equivalents, any three of the four formulas or substances may be chosen as the components, if negative percentages are permitted, whereupon pure CB, for example, $= AB + CD - AD$, in terms of the latter three formulas or substances as the components. The simple or additive ternary system is the more frequent and important case, and it is discussed in Chapters X–XIV; the reciprocal ternary system is discussed in Chapter XV.

With four independent variables — P , T , and two composition terms — graphical representation in a single figure is possible only with one of the four variables constant. (Such restriction would not apply in so-called “analytical methods,” algebraic or non-graphical, for the treatment of multicomponent systems.¹) A 3-dimensional figure is therefore used for the system either at constant P or at constant T . One of the variables, P , T , is taken as an axis perpendicular to a composition plane, the plane most commonly used and giving in general the greatest clarity being the equilateral triangle. The 3-dimensional figure is then a $(P/c)_T$ or $(T/c)_P$ triangular prism, and a horizontal section is the isobaric, isothermal section of the system, the composition triangle itself.

In this composition triangle each corner represents a pure component, each side a binary composition, and the interior a ternary composition. The percentage of each component at any point is measured either by a perpendicular or by a parallel to the opposite side. In either case the scale will be the same for the three components only in an equilateral triangle, as in Fig. 10–1. Now if the side of the triangle is the unit ($= 100\%$) the

¹ See, for example, G. W. Morey, *J. Phys. Chem.*, **34**, 1745 (1930); L. A. Dahl, *ibid.*, **52**, 698 (1948).

percentage of each component at the point Y is the parallel to the opposite side: aY for A, bY for B, and cY for C. If the altitude is the unit, each percentage is the perpendicular to the opposite side: $a'Y$, $b'Y$, $c'Y$.

In general any triangle may be used, provided each side is divided into the same number of units (100), as in Fig. 10-2. The percentage of each component is again given by one of the parallels (read on its appropriate

scale) to the opposite side. The percentage of B in Y, for example, is bY on the AB scale or $b'Y$ on the CB scale.

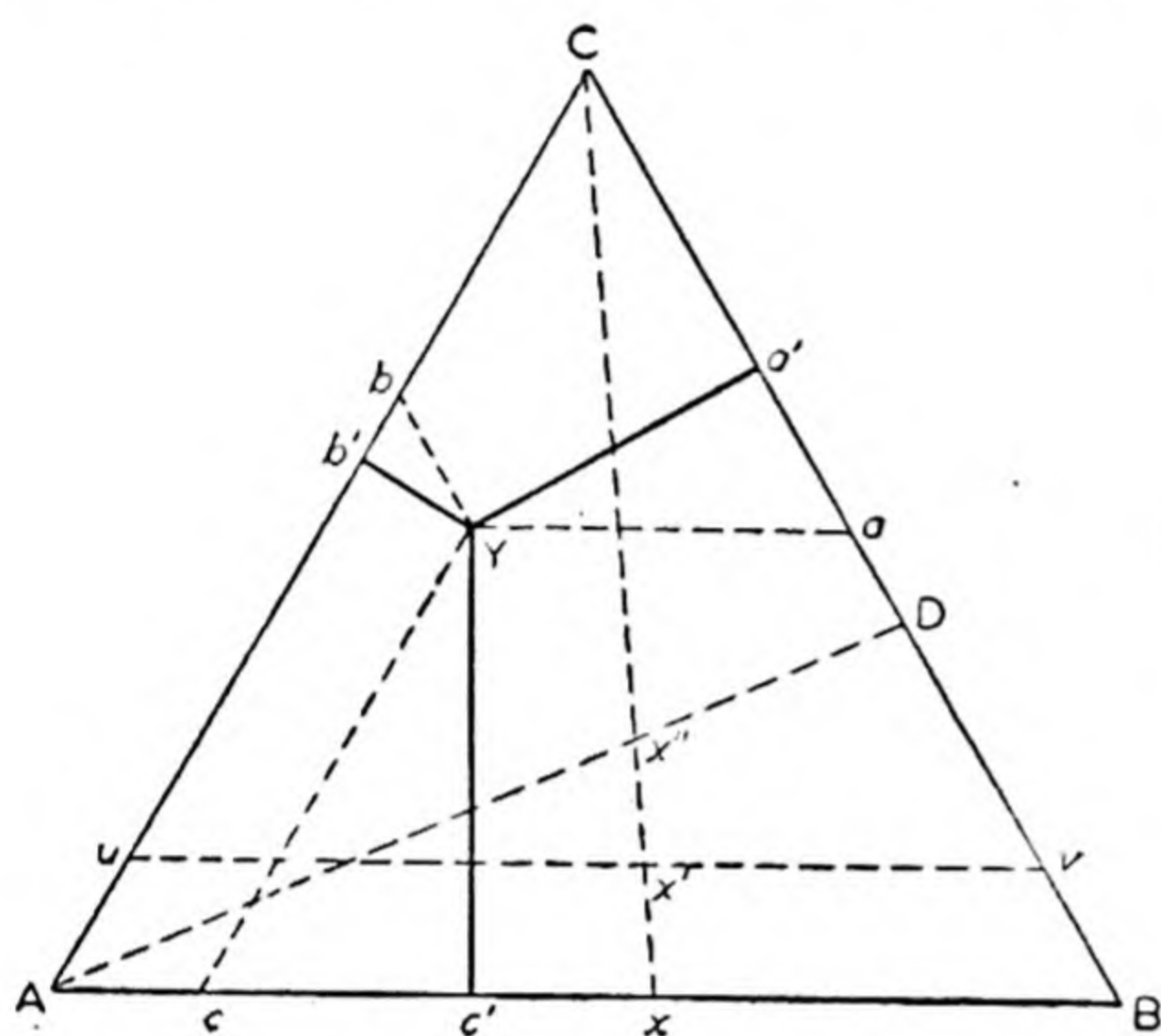


FIG. 10-1. Composition triangle.

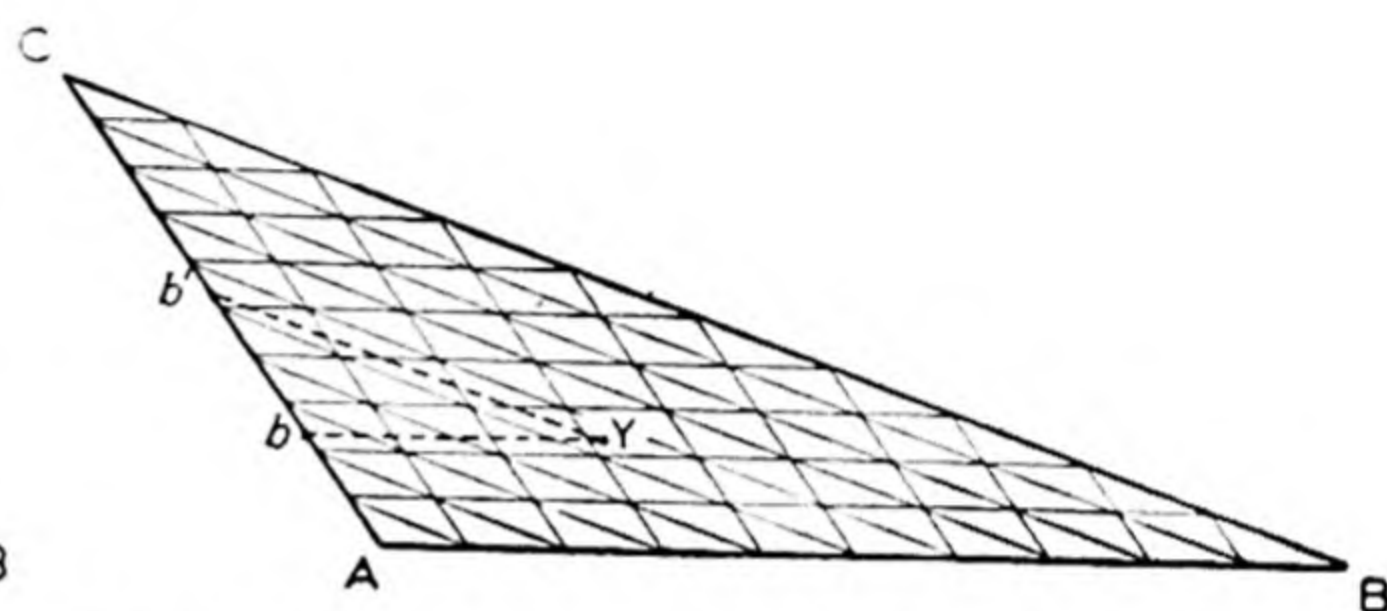


FIG. 10-2. Scalene composition triangle.

Some useful features of the composition triangle, whether equilateral or not, are to be noted:

1. The ratio of two components is constant along a line through the third; the ratio A/B is constant along the line Cx , since $xB/xA = x'v/x'u$, the line uv being parallel to AB. While uv is a line of constant percentage of C, the line Cx represents constant ratio of A to B. Upon addition of C to the composition x' the total composition moves on the line $x'C$ toward C; on removal of C from x' (as by evaporation of C) the composition moves along $x'x$ toward x .

2. The composition of a point, such as x' , may therefore be expressed either in terms of % A and % B (any two components) or in terms of % C and the ratio A/B, as the independent composition variables.

3. The ratio of A to any fixed composition such as D on the opposite side is similarly constant along a line through either of the other corners. This means that, if the compositions in the arbitrary triangle ACD are expressed in terms of A, C, D, then $x''D/x''A$ is the constant ratio of A to D on the line Cx'' and the same ratio holds on the line $x''B$ for the triangle ABD.

4. This principle can be extended whenever necessary or convenient for a sub-triangle in the actual ABC diagram.

5. If two complexes or compositions are mixed, the total composition lies

on the line joining them, at a point dividing that line into segments inversely proportional to the ratio of the quantities of the original complexes taken. This is the same as the principle of tie-line segments already used in 2-phase binary equilibria.

6. This is merely a special case of the principle of center of gravity. If a complex, such as point Y of Fig. 10-3, exists in three phases, such as a, b, c , the relative amounts of the three phases are found as follows:

$$\frac{c}{a+b} = \frac{Yz}{Yc},$$

and $\frac{a}{b} = \frac{bz}{az}.$

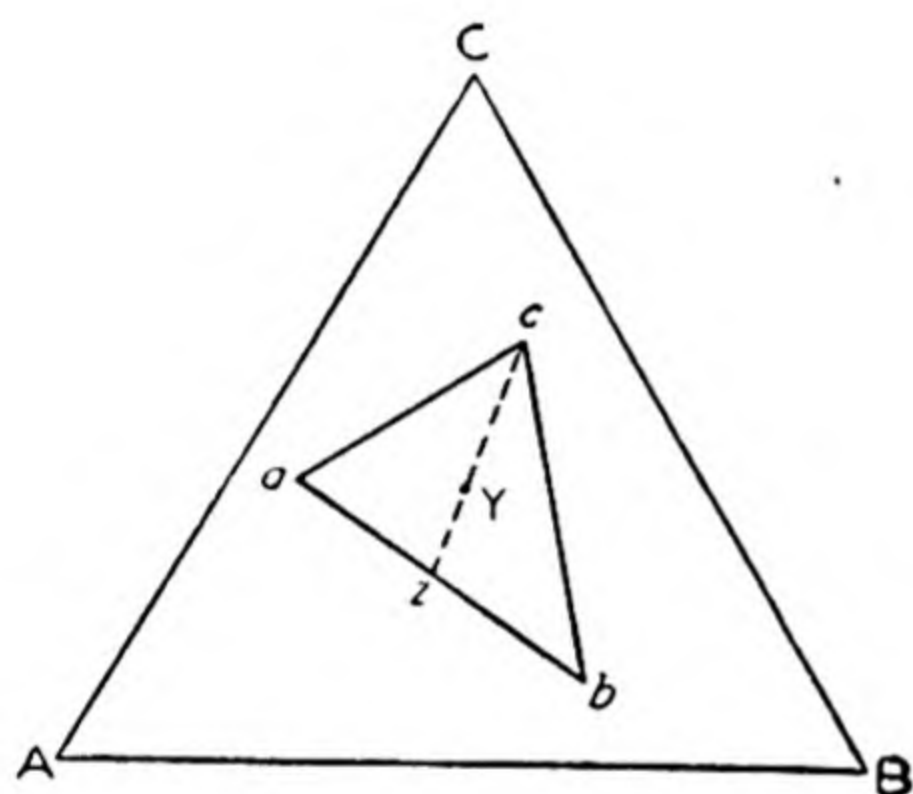


FIG. 10-3. Three-phase complex.

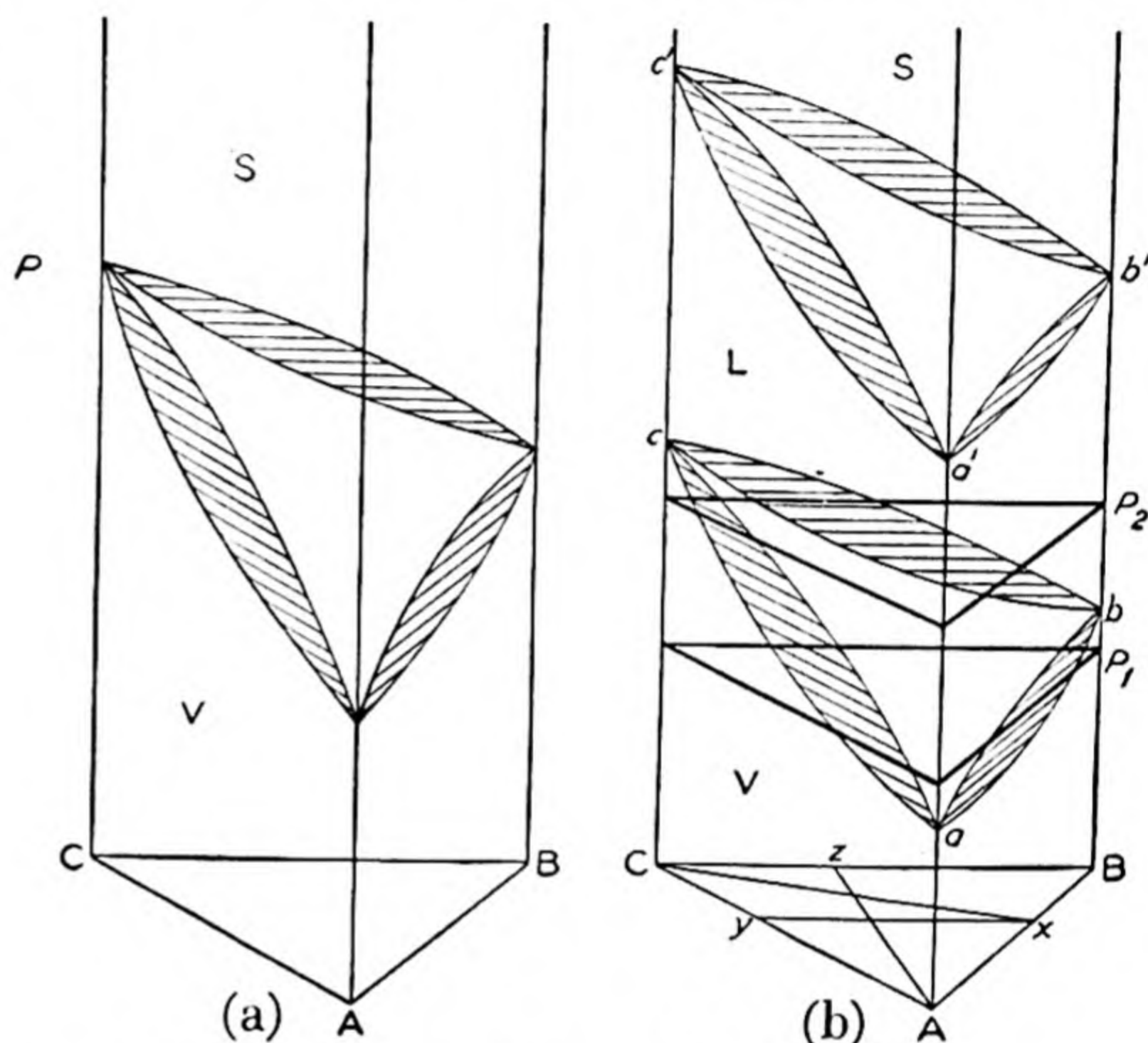


FIG. 10-4. Isothermal transition loops.

With T (or P) as an axis perpendicular to this composition triangle each face of the prism represents the $(T/c)_P$ or the $(P/c)_T$ section of a binary system. Hence the importance of the systematic study of the binary sections. In many simple cases, the interior of the ternary prism involves very little that is new, if the relevant binary sections are already known. If T is the vertical axis and the pressure is that of the open air, then the sides are the binary open air condensed T/c diagrams already discussed. The T/c prism may be used, in other words, as the T/c plane in the binary case, to represent the equilibria of condensed phases either under the pressure of the system or in the open, under atmospheric pressure, without recording the actual pressure and without determining or plotting the vapor composition. Every horizontal section of such a prism is then a "condensed" ternary isotherm; on this isotherm the vapor pressure varies from point to point — as does also, then, the total pressure unless the system is open to the air.

B. Phase Transition Surfaces

In the $(T/c)_P$ or $(P/c)_T$ prism, a ternary phase of variable composition (V, L , or S) is represented by a space, trivariant at either constant P or

constant T . A 2-phase equilibrium is represented by a space filled with 2-phase tie-lines, isothermally or isobarically bivariant. These tie-lines are horizontal, both in T/c and in P/c , but they may have any direction in the composition plane. If one of the two phases is of fixed composition (a pure solid) then all the tie-lines converge, whatever the T or P , at the vertical line representing the pure solid; their other extremities then generate a smooth surface representing the solubility surface of the fixed phase. A 3-phase (isothermally or isobarically univariant) system consists, at fixed T and P , of a 3-phase triangle, as in Fig. 10-3; any of the three phases may or may not be variable in composition. With changing T (or P) this triangle generates a 3-edged space of 3-phase equilibrium, univariant in $(P/c)_T$ or $(T/c)_P$. A 4-phase system results by the intersection of four such 3-phase equilibria. This is referred to as an isothermally or isobarically invariant "point," although it will be a plane containing four different phases. In the "condensed" T/c prism, in which the vapor, though present, is not plotted, such a system will actually be an invariant, quintuple point. As usual, if the system is open to the air, the concentrations, temperature, and vapor pressure will vary, because of the effect of the atmosphere and its pressure, from the values for the true quintuple point at the pressure of the system, to some slight, often negligible, extent, as explained for quadruple points in binary systems.

As in the case of binary systems, we shall refer to the transitions $S \rightleftharpoons L$, $S \rightleftharpoons V$, and $L \rightleftharpoons V$ as the transition $Ph\ 1 \rightleftharpoons Ph\ 2$. In the present chapter we shall consider only the simplest case, in which each of the phases, S , L , V , is continuous, with no miscibility gap, in the ternary system. If, in addition, all three binary loops, S/L , S/V , and L/V , have no maximum or minimum in P or T , and if all three S/L loops have a positive P/T slope, then the isotherm, or the $(P/c)_T$ prism, of the ternary system is schematically the diagram of Fig. 10-4: (a) at T below, (b) above, the triple points of the components. In Fig. 10-4 (b) the loop $a-b$ is the L/V loop of the binary system $A-B$, a being the vapor pressure of liquid A at the T of the prism; and the loop $a'-b'$ is the S/L loop of the same binary system, a' being the melting P of solid A . The lower binary curves joining a , b , c are the binary limits of the *ternary vaporus*, a curved surface upon which ternary vapor begins to condense to give a liquid of different composition defined by the *ternary liquidus*, a surface bounded by the binary liquidi. The S/L loop or equilibrium is similarly defined by two ternary surfaces, a *liquidus* and a *solidus*, meeting at the points a' , b' , c' .

Again, as for binary systems, if these prisms are turned upside down, they give the general forms of the isobars of the system, or the $(T/c)_P$ prism: Fig. 10-4(b), the S/L or freezing point surfaces at low T and the boiling

point (L/V) surfaces at higher T (for P above the triple points); and Fig. 10-4(a), the S/V or sublimation surfaces for P below the triple points. This principle holds as long as the S/L loops have positive P/T slopes and as long as there is no pressure maximum in a solubility curve (such as seen in Figs. 5-11, 5-15, 7-26, 7-34), for with such a pressure maximum the solubility curve (or surface in the ternary system) is cut only once in the P/c prism but twice in the T/c prism.

What we here have to say, therefore, covers generally — *mutatis mutandis* with care — a variety of phenomena, all fundamentally the same in phase rule significance and representation. With increasing P the transition is (normally) $Ph\ 2 \rightarrow Ph\ 1$, and with increasing T , $Ph\ 1 \rightarrow Ph\ 2$; and all six cases, that is, three transitions with respect to change of either T or P , can be treated as schematically the same, for generality and economy.

The shape of a ternary transition loop or surface-pair, even in this simplest case of continuous phases without miscibility gaps, will vary considerably from system to system, in view especially of the variety possible in the three binary loops. The two surfaces ($Ph\ 1$ and $Ph\ 2$) may be both convex or both concave, toward the base of the prism, or of opposite curvature. The maximum (or minimum) of a surface is always a point of contact of the two surfaces of the transition. The points representing pure components are always points of contact, of course, whether or not they represent maxima or minima of the surfaces. The maximum or minimum of a surface may be the transition P (or T) of a pure component (as is possible in Fig. 10-4), or a binary maximum or minimum (a point on the $Ph\ 1/Ph\ 2$ loop of a binary system), or a ternary maximum or minimum. A ternary maximum, for example, in Fig. 10-4, would give a dome-shaped surface falling away

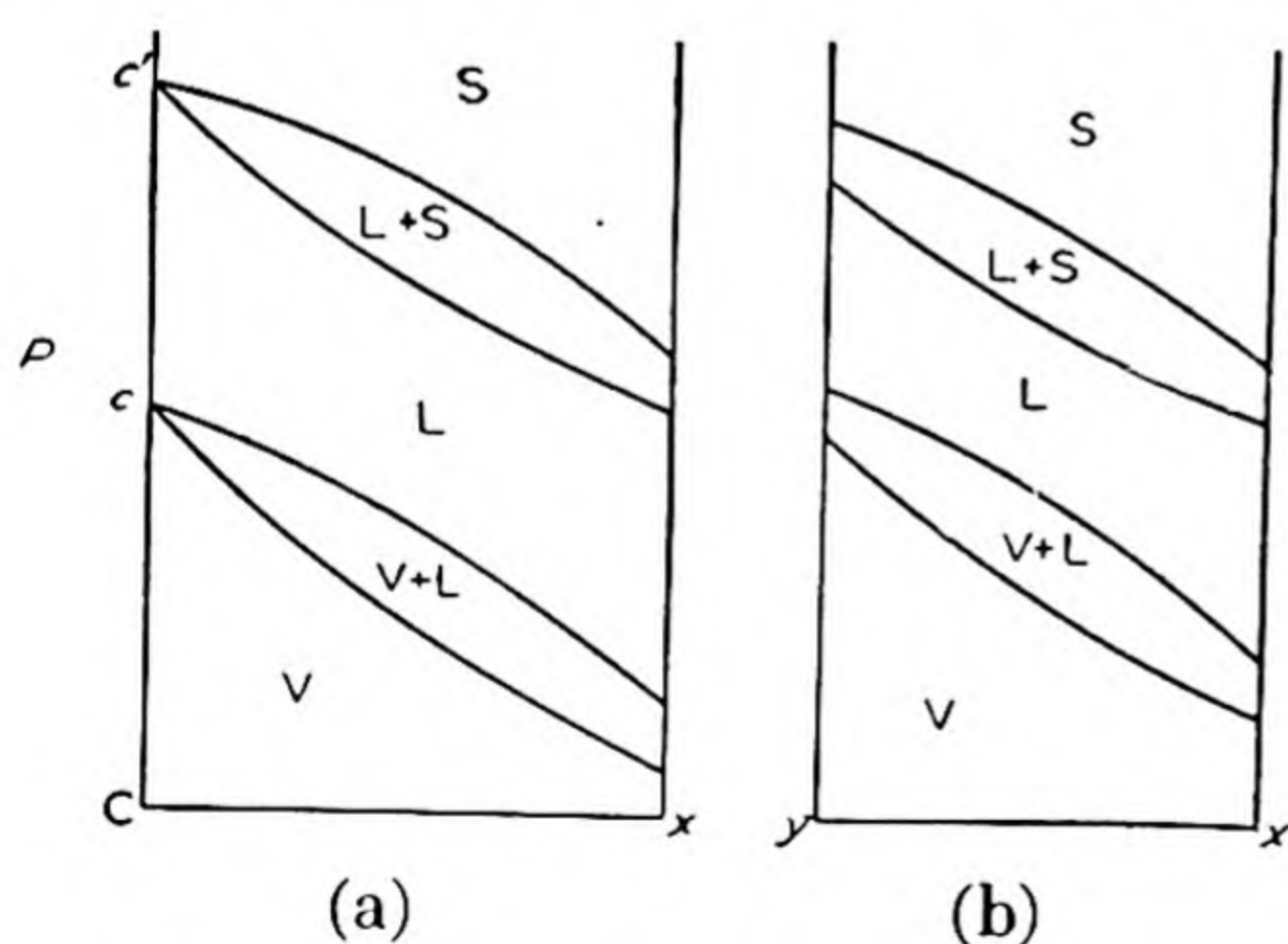


FIG. 10-5. Vertical sections of Fig. 10-5(b).

on every side to the binary curves. (Such a ternary point is sometimes called an "absolute" maximum or minimum.) In the liquid-vapor transition, this would be a ternary azeotrope; in the solid-liquid transition, the system may have a ternary composition of minimum freezing point.

Vertical sections of the P/c prism of Fig. 10-4 differ from binary P/c sections in that the two curves of a loop do not meet at the edge of the

section. If the system has no ternary maximum or minimum, Fig. 10-5(a) shows the section Cx , and Fig. 10-5(b) the section yx of Fig. 10-4(b).

Furthermore, the coexisting phases in a loop are not given simply by horizontal tie-lines in the section. Mixtures of y and x falling in the S/L loop of Fig. 10-5(b) give a liquid phase with composition behind the plane of the paper toward the BC side of the prism, because a' is the minimum of the surfaces, and the coexisting solid would lie in the opposite direction, toward A.

Horizontal sections (isothermal isobars), as at P_1 , P_b , and P_2 , shown in Fig. 10-6, do contain the 2-phase tie-lines, on the other hand.

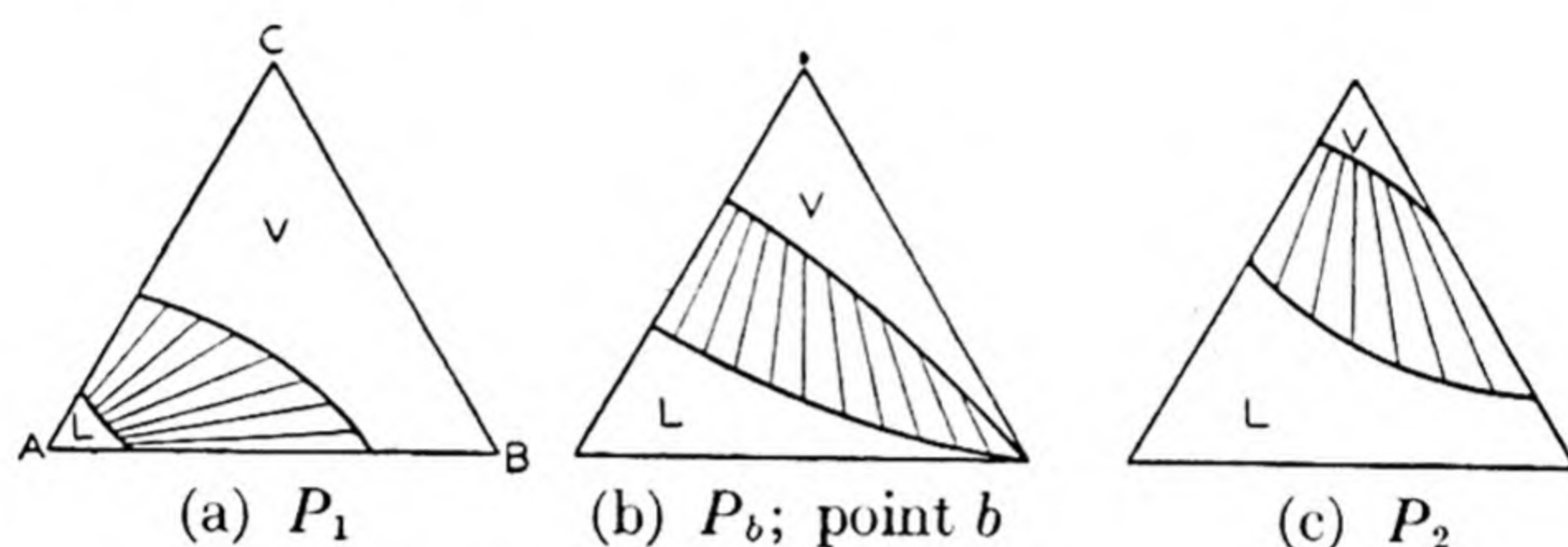


FIG. 10-6. Horizontal sections of Fig. 10-5(b).

Let us now suppose that the temperature of Fig. 10-4(b) is above the critical point ($L = V$) of A, but below the critical points of B and C. Then the ternary liquid-vapor surfaces will not reach the pure A corner, and a section such as zA appears as in Fig. 10-7. At some point such as K, there will be the critical identity of ternary L and V phases, and the curve generated by such points is the ternary critical curve, running from the AC face to the AB face, for the specified temperature of the P/c prism. With the critical identity between liquid and vapor phases, the ternary system in two phases is bivariant, or isothermally univariant, by restriction. The 3-dimensional critical curve of the P/c prism generates, with varying T , a "surface" in the 4-dimensional relations of the system.

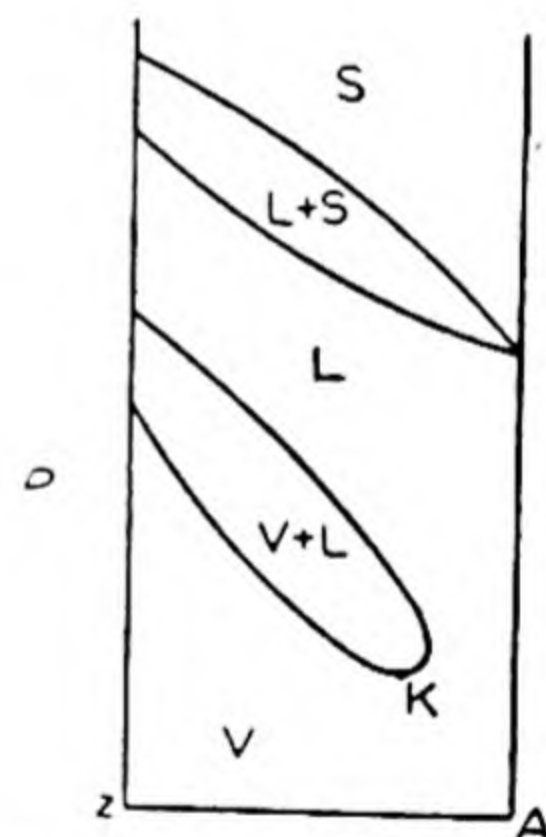


FIG. 10-7. Vertical section at temperature above critical point of A.

If all three binary L/V loops are azeotropic, at the T of the prism, with P -maxima, and if in addition there is a ternary "absolute" maximum, or ternary azeotrope, near the C corner, then the isobar just below the ternary maximum appears as in Fig. 10-8(a). With decreasing P , the subsequent isobars, b , d , e , indicate pressures below the azeotropic maxima of the binary systems B-C, C-A, A-B successively, these maxima being assumed to occur above the vapor pressures of all three components. Fig. 10-8(c) is an isobar

at the azeotropic maximum of the A-C system. A section through C and the ternary azeotrope would appear as in Fig. 10-9(a), while a section passing through C but slightly missing the ternary azeotrope is shown in Fig. 10-9(b).

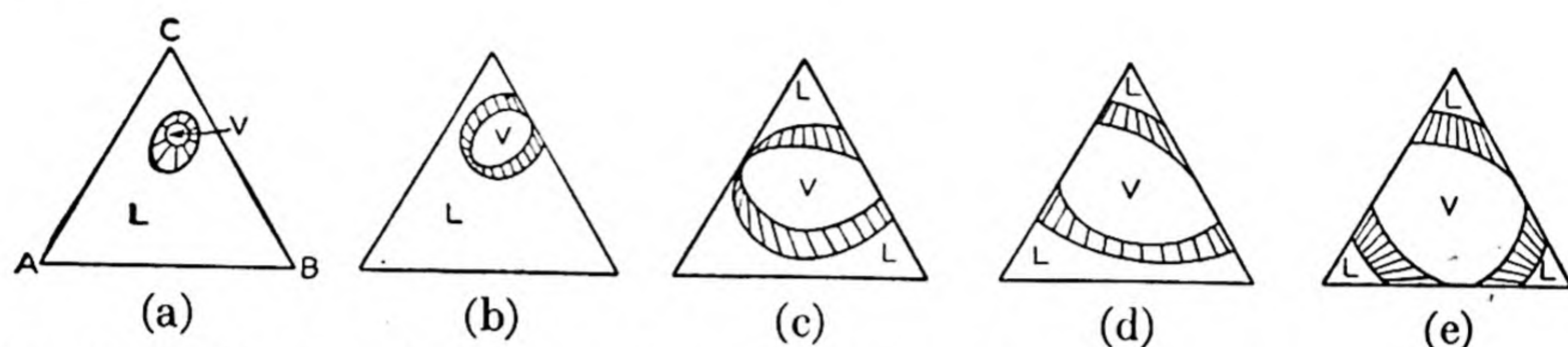


FIG. 10-8. Horizontal sections for system with ternary azeotropic P -maximum.

If the ternary liquid is heated at constant P , it begins to vaporize on reaching the liquidus, that of Fig. 10-4(b) turned upside down, the compositions and relative proportions of the phases L and V being given by tie-lines which can only be shown by a series of isotherms or other devices.

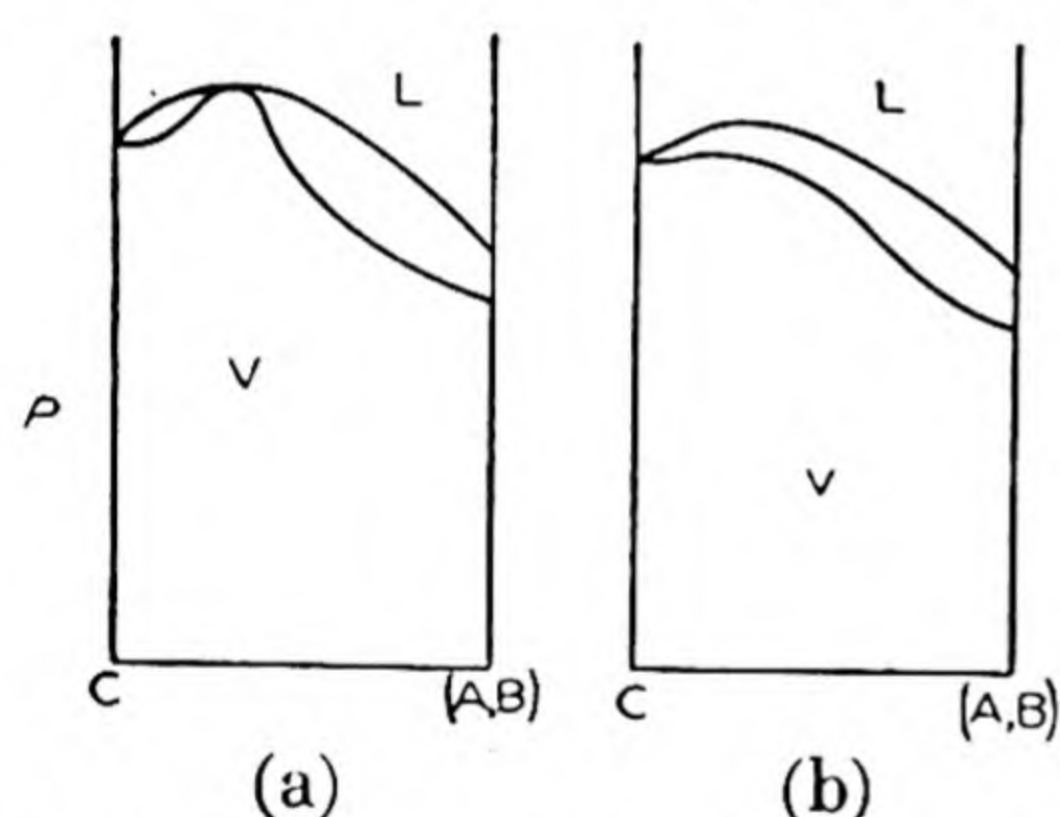


FIG. 10-9. Vertical sections for ternary azeotropic P -maximum.

The initial vapor differs in composition from the original liquid (unless this happens to be the azeotropic composition), but, as the liquid disappears, the vapor approaches the composition of the original liquid, since the total composition is fixed. The same happens if ternary liquid is cooled at constant P , to give a ternary solid solution. In either case there is a transition range of boiling or of freezing, the range being the vertical temperature interval between the $Ph\ 1$ and $Ph\ 2$ surfaces of the transition, for the given composition and specified P .

During the equilibrium solidification process of a ternary liquid of composition \mathbf{P} , when the system is heterogeneous and lies in the space between the transition surfaces, the composition of each phase follows a curved course on the appropriate phase surface; the liquid composition is \mathbf{P} at the start of the solidification, whereas the solid composition is \mathbf{P} at the end. At some specified intermediate temperature T_1 within the transition or freezing range, the two phases, with compositions L_1 and S_1 , lie at the extremities of a horizontal, isothermal tie-line, $L_1\mathbf{P}S_1$, which always passes through the vertical line, in the $(T/c)_P$ prism, representing the fixed total composition \mathbf{P} of the complex. The same tie-line gives the phase compositions, moreover, at the temperature T_1 , for any total composition lying on the line L_1S_1 . From the point L_1 of the liquidus surface there is, in other words, only one

equilibrium tie-line, L_1S_1 , to the solidus surface, indicating the ternary solid solution S_1 in equilibrium with the given ternary liquid L_1 .

In every case the liquid and solid compositions will then change upon further cooling. The course followed by each phase on its appropriate surface, however, will depend upon the total composition P , for while both phases are changing in composition the condition must still be met in every case that the tie-line joining them must pass through P . Hence although there is but one equilibrium tie-line for any one point on the liquidus surface, the path followed by the liquid on further cooling under conditions of complete equilibrium is not unique, being a function of the total composition of the 2-phase system and being restricted only in the sense of having to proceed toward a part of the surface representing lower temperature. It is therefore impossible to represent *equilibrium* crystallization paths on such a liquidus surface, for there is an infinite number passing through any point. The same is true for vaporization paths on a liquidus, condensation paths on a vaporus or melting paths on a solidus, for transitions in complete equilibrium.

This is the case, at any rate, when both phases involved in the transition are of variable composition, as in the present condition of complete miscibility in both phases. If, however, one of the phases is a pure solid of fixed composition, then the equilibrium path followed by the liquid at any given point of the liquidus surface will be unique since the tie-line, with one end fixed at the composition of the pure solid phase, cannot change its direction during the separation of that phase upon cooling or during its dissolving upon heating.

We consider next the condition in which the phase formed by the transition is not allowed to readjust its composition to maintain complete equilibrium but is effectively removed during the process. If the phase formed by the transition (V on boiling, for example) is effectively removed as it is formed, then, as in the distillation of binary liquid, there will not be a definite transition range for a particular complex, but the boiling point of the residual liquid rises instead toward the absolute maximum of the boiling point surface, which may be the boiling point of a pure component, a binary azeotrope, or a ternary azeotrope. The ternary azeotrope, whether of the maximum or of the minimum type, again sets a limit to separation by distillation.² The same considerations hold for the freezing surface of the ternary system. If the solid solution formed upon cooling the ternary liquid does not readjust its composition according to the equilibrium tie-lines between liquidus and solidus, it may be considered effectively removed

² For collected data on the azeotropes of binary, ternary and higher systems, see L. H. Horsley, *Anal. Chem.*, **19**, 508 (1947); for supplement, *ibid.*, **21**, 831 (1949).

from the system just as the vapor is removed during distillation of a liquid. As a result the freezing point range is no longer the T -interval mentioned previously; but the freezing point of the residual liquid now proceeds toward the absolute minimum of the ternary system. If the liquid is not consumed during the process, the freezing point will reach some definite point such as that of a pure component, a binary liquid of minimum freezing point, or a ternary "absolute" minimum.

The course of the composition of the residual liquid, during its progress to a maximum boiling point or to a minimum freezing point during distillation or during such freezing with effective removal of solid, may be called the boiling point path or the crystallization path, respectively. The same considerations apply, of course, for the solid-vapor transition and on either a P/c or a T/c surface, in all cases, but the boiling point and crystallization phenomena are the most important. The boiling path proceeds to a temperature maximum; the crystallization path, to a temperature minimum. The relations in either case may be summarized by direction curves on the composition plane, as in Fig. 10-10, in which all three binary loops and the

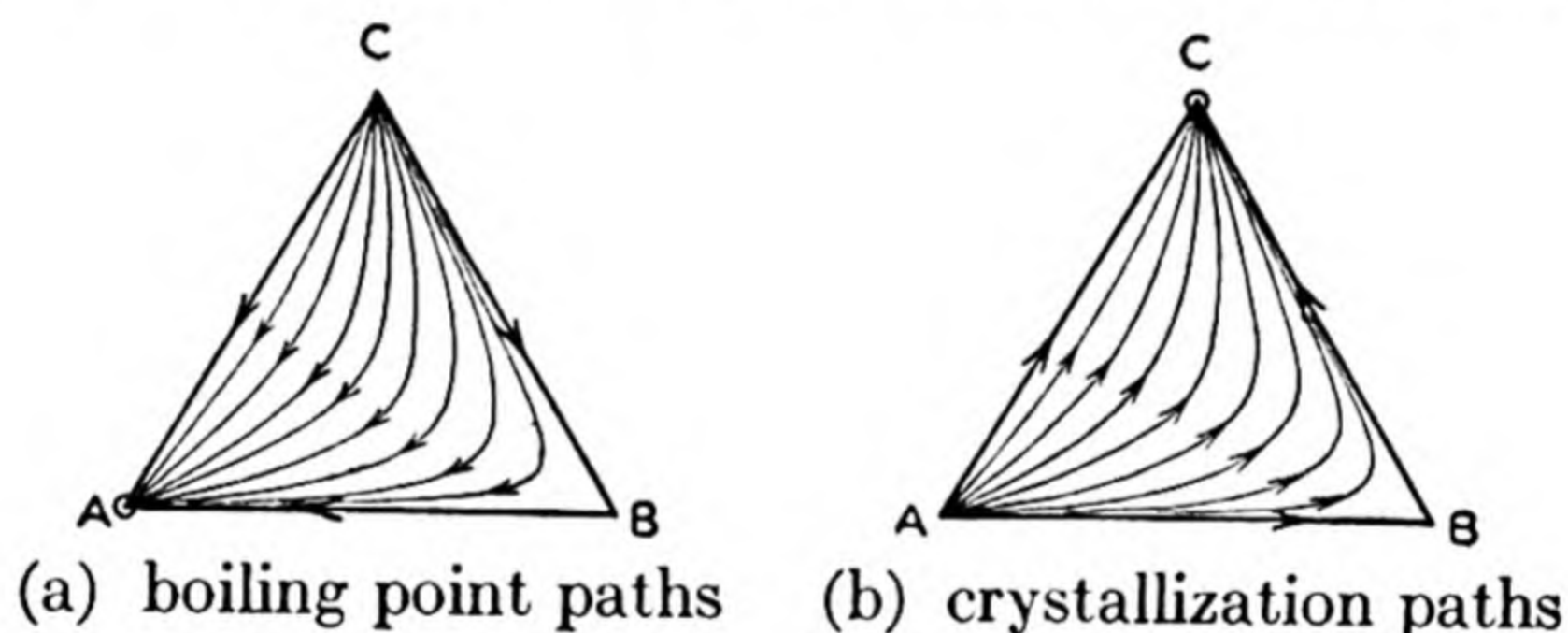


FIG. 10-10. Liquidus surface of simple system.

ternary surfaces are assumed to be of the simple, ascendant type. The boiling points (or freezing points) are assumed to be, as in Fig. 10-4 (b) turned upside down to give the T/c prism, in the order $A > B > C$, so that A is the absolute maximum and C the minimum of the ternary transition. All boiling paths therefore rise from C to A, in Fig. 10-10(a), and all crystallization paths fall from A to C, in Fig. 10-10(b). These diagrams show only the relative temperatures of various points in the (isobaric) ternary liquidus. The actual temperatures may be added in the form of isothermal contours, these contours being roughly concentric, in this case, at either A or C, depending on the convexity or concavity of the surface involved. Qualitatively, Fig. 10-10(a) also gives the condensation paths for the isobaric cooling of vapor, if the liquid is assumed to be removed as it is formed. But then the direction would be reversed, from A to the minimum at C, and furthermore the paths would not be exactly the same, since the curvatures of the two surfaces of a phase transition, as mentioned earlier, are not the same.

At any rate, one such diagram applies schematically to any $Ph\ 1 \rightleftharpoons Ph\ 2$ transition, with the condition that the transition $Ph\ 1 \rightarrow Ph\ 2$ occurs with increasing T at constant P , and with decreasing P at constant T . A few examples of the various shapes of surfaces are therefore represented in Fig. 10-11.³ In 10-11(a), as a boiling point diagram, m_1 is a binary aze-

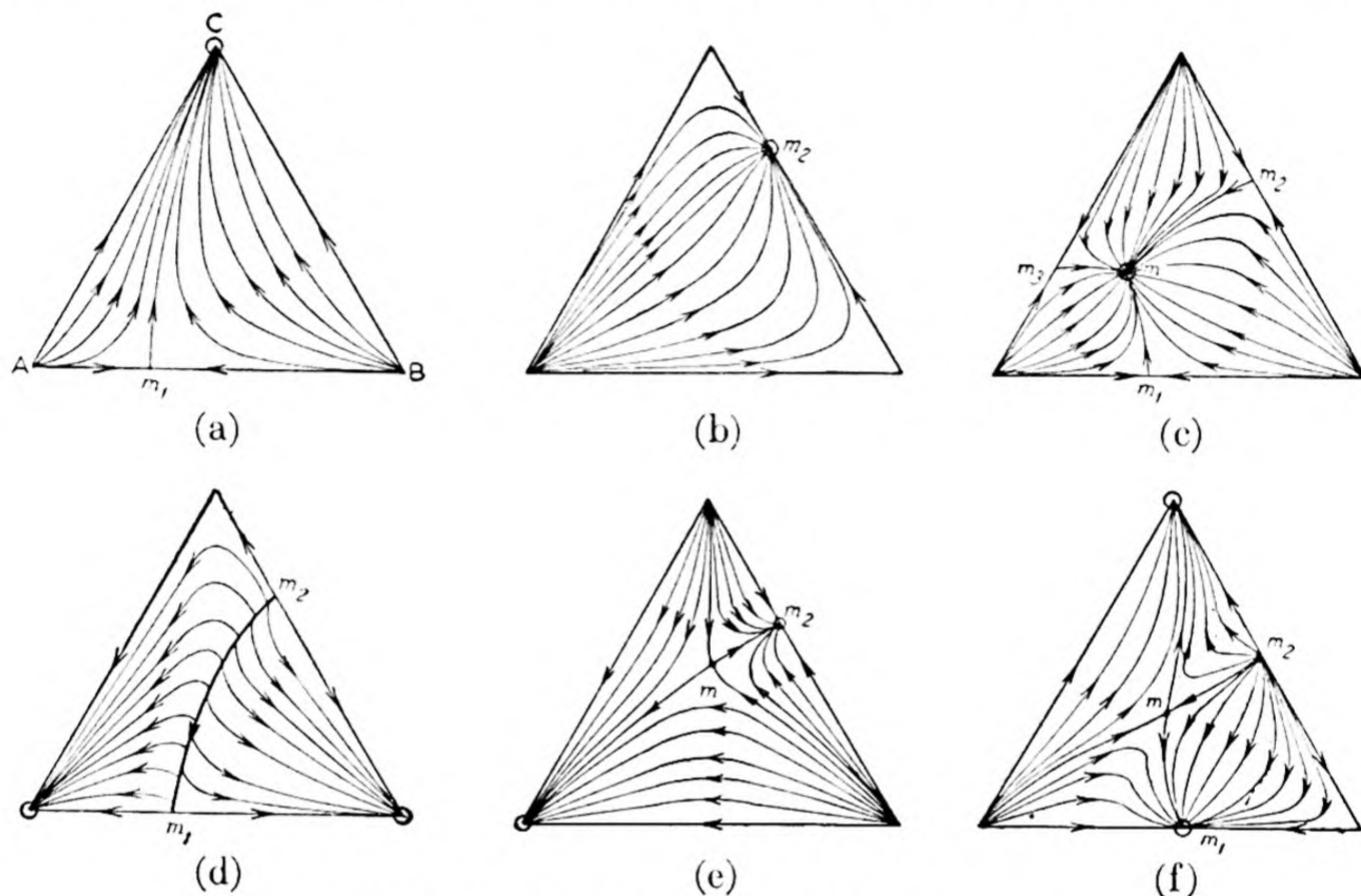


FIG. 10-11. Various shapes of the liquidus surface.

otrope (T -maximum) in the A-B system, and its T is $< C$, with $C > B$ and $C > A$, but the relation of A to B is not shown. As a freezing point diagram, m_1 would be the minimum in the freezing point curve of A-B, but $> C$, with $C < B$ and $C < A$. In 10-11(b), as a boiling point diagram, m_2 is a T -maximum in B-C, and $> A$, with $A < C$ and $A < B$. In 10-11(c), as a freezing point diagram, m_1, m_2, m_3 are binary minima, m the ternary minimum.

In 10-11(d) as a boiling point diagram (liquidus surface) m_1 and m_2 are minimum boiling binary azeotropes, $m_2 < m_1$ and $A > C$. The line m_1m_2 is therefore a minimum trough on the liquidus surface. The corresponding minimum trough of the vaporus surface while isothermal with m_1m_2 of the liquidus will not coincide with it in composition. Although such minimum troughs and maximum ridges joining binary azeotropes are sometimes called "azeotropic troughs or ridges," there is no azeotropic point on them at all. A ternary azeotrope, with identity of composition of $Ph\ 1$ and $Ph\ 2$, a point

³ For examples of ternary isobaric boiling point diagrams, see *I. C. T.*, III, 306-8.

of contact of the *Ph 1* and *Ph 2* surfaces, occurs only at an absolute minimum or maximum. If m_1 and m_2 were maximum boiling azeotropes, the system would have a ridge of maximum temperature on the liquidus, between m_1 and m_2 . This figure is schematic for the liquidus of the boiling point diagram of the system benzene(A)–ethyl alcohol(B)–carbon tetrachloride(C);⁴ if the arrows are reversed the same diagram represents the vapor pressure of the system at constant temperature.⁵ With the arrows reversed the diagram also represents schematically the liquidus of the freezing point diagram of the system palladium (A)–nickel(B)–gold(C), so that the single crystallization end-point is then m_2 .⁶ The system *p*-chlorobromobenzene (A)–*p*-dichlorobenzene(B)–*p*-dibromobenzene(C) differs from this in its freezing point surface only in that the order of the freezing points of C and A is reversed, with $C > A$.⁷

In 10–11(e), as a crystallization diagram, m_2 is a minimum in B–C, but whether m_2 is $>$ or $<$ A, the curve Am_2 is assumed to have a maximum in it at m ; this maximum is furthermore assumed lower than both C and B. In 10–11(f), as a boiling diagram, m_2 is a minimum in B–C, m_1 a maximum in A–B; $A < C$; m is a maximum between A and m_2 , but minimum between C and m_1 . The shape of the surface is then that of a saddle, between A and m_2 , and the point m is called a “saddle point,” both in 10–11(e) and in 10–11(f). Although a saddle point is not an “absolute” maximum or minimum it is still a point of contact of the surfaces of *Ph 1* and *Ph 2*. The circled points in these diagrams (Figs. 10–10 and 10–11) are called vaporization end-points or crystallization end-points.

C. Miscibility Gaps in Solid or Liquid

In this section we shall consider the occurrence of miscibility gaps in the space representing ternary solid or ternary liquid, but not their intersection with any phase transition surfaces (S/L, S/V, L/V). For clarity and familiarity, we shall speak of the *MG* in the liquid state, but the relations, of course, hold equally for the solid state.

1. Miscibility Gap in One Binary System (A–B)

If, at the *P* of the *T/c* prism, there is complete miscibility in the pairs A–C and B–C, but a *MG* in the pair A–B, with upper and lower critical

⁴ F. A. H. Schreinemakers, *Z. phys. Chem.*, **48**, 257 (1904); see also A. N. Campbell and W. J. Dulmage, *J. Am. Chem. Soc.*, **70**, 1723 (1948).

⁵ Schreinemakers, *loc. cit.*

⁶ W. Frankel and A. Stern, *Z. anorg. Chem.*, **166**, 161 (1927).

⁷ G. Bruni and F. Gorni, *Atti R. Accad. Lincei*, **8**, 212 (1899); see also A. N. Campbell and L. A. Prodan, *J. Am. Chem. Soc.*, **70**, 553 (1948).

solution points, the schematic relations are those of Fig. 10-12. In this figure it is assumed that component C lowers the upper critical solution temperature (K_1) and raises the lower (K_2), so that the critical solution curve (ternary) from K_1 to K_2 has no ternary maximum or minimum of temperature. This is a 3-dimensional curve, the ratio of A to B being variable along it. The space hollowed out by the *MG* is a ternary 2-phase (isobarically bivariant) equilibrium filled with isothermal 2-phase tie-lines.

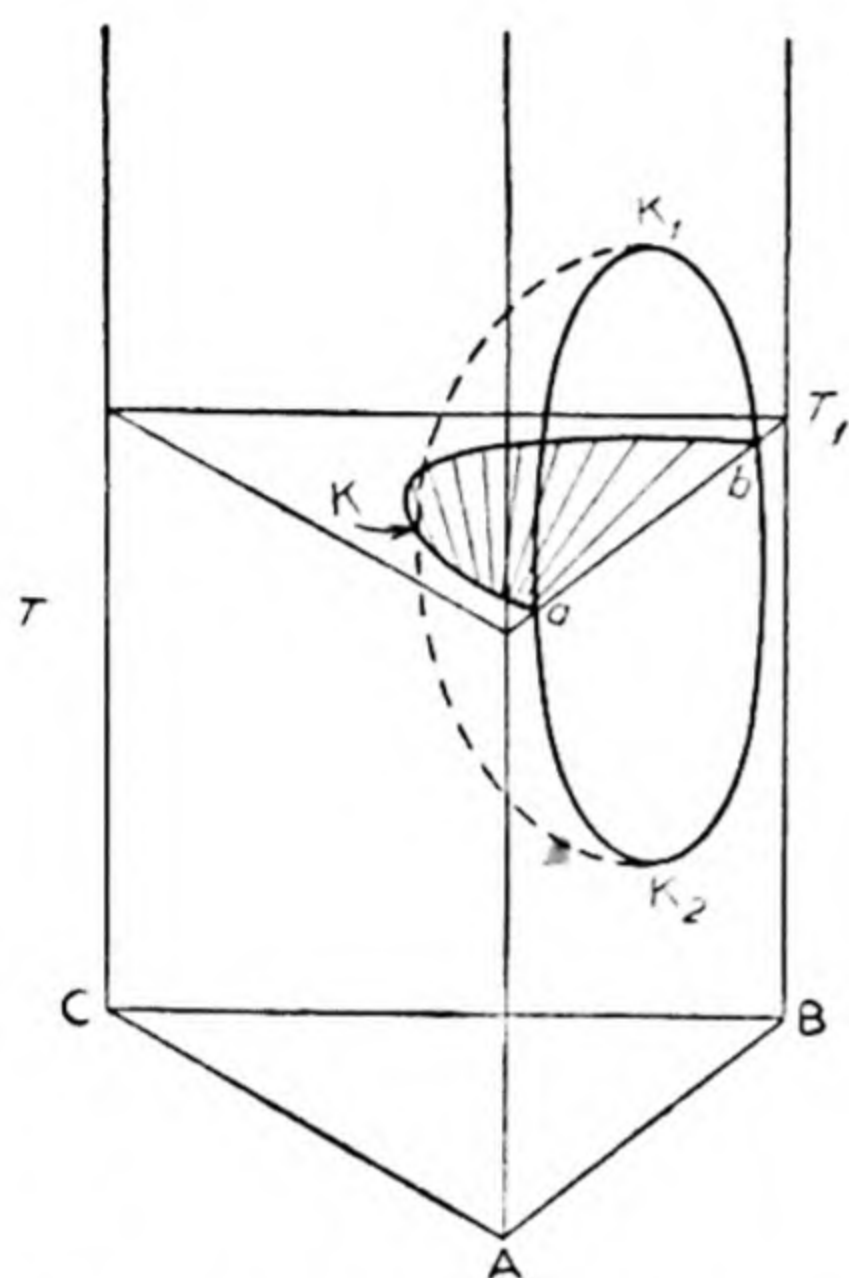


FIG. 10-12. Miscibility gap in system A-B.

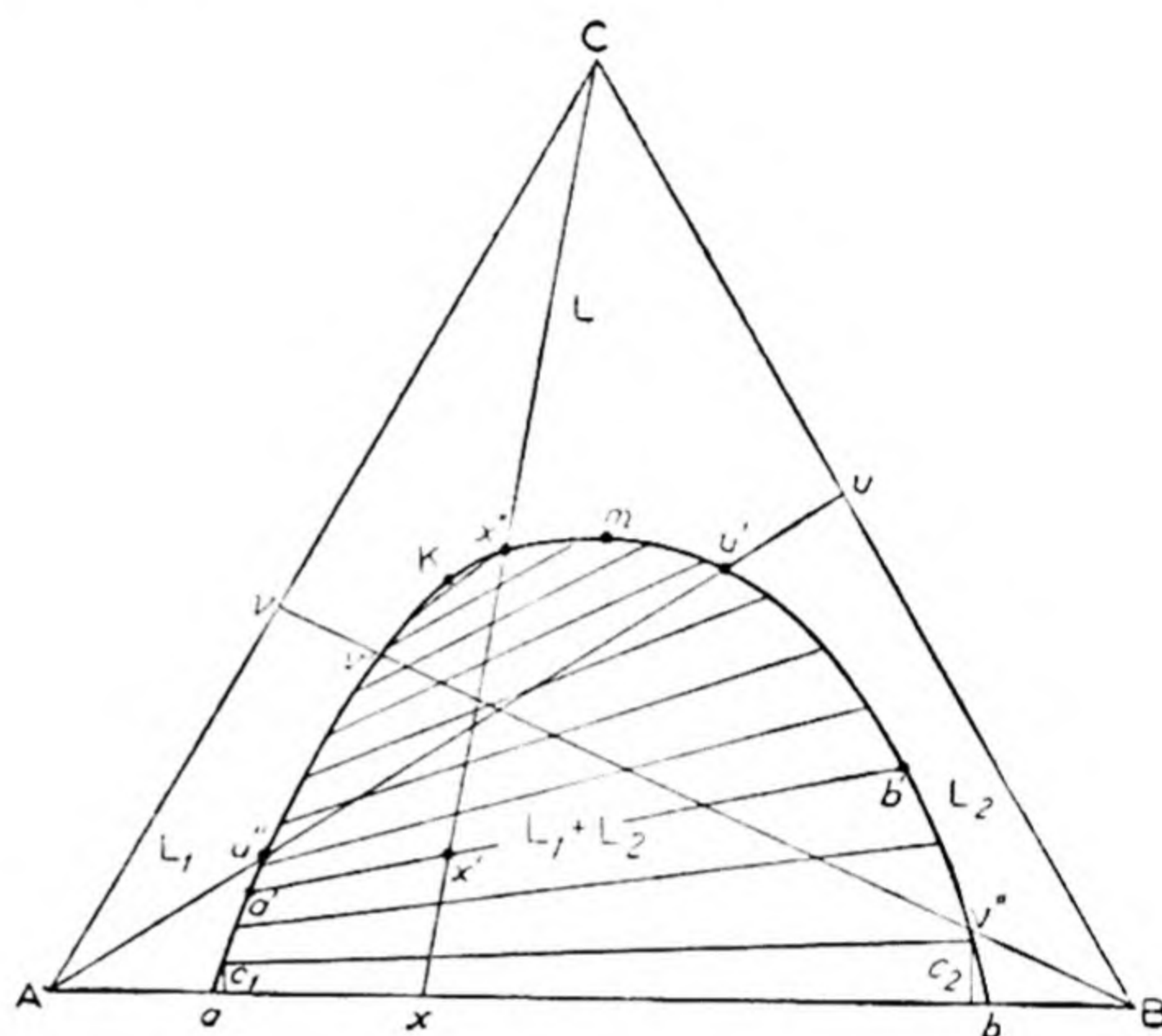


FIG. 10-13. Horizontal section of Fig. 10-12.

At any T , such as T_1 (Fig. 10-13), the tie-lines start from the binary tie-line ab ; as component C is added, the conjugate liquids become ternary, and the tie-lines join points on the isothermal section aKb of the *MG*, called the binodal curve, or the binodal solubility curve, because there are two related values of solubility on it; this curve is merely a section of what may be called the binodal surface of the system, the wall of the *MG* of Fig. 10-12. As the tie-lines proceed into the ternary system, they are no longer parallel to the side AB , and they finally become shorter and vanish to a point on the critical curve K_1K_2 , the point K for the isotherm. This point, the isothermal (and also isobaric) critical solution point, or the **plait point**, is not necessarily the maximum of the binodal curve in respect to percentage of C, point m . The region of the isotherm outside the binodal curve, which is smooth and continuous from a to b , is homogeneous ternary liquid. Fig. 10-13 may be taken schematically as the system chloroform (A)–water (B)–acetic acid (C) at room temperature.⁸

⁸ C. R. A. Wright, *Proc. Roy. Soc.*, **49**, 174 (1891); **50**, 375 (1892).

As to whether C increases or decreases the mutual solubility of A and B at the specified T and P , this depends on the meaning attached to the word "concentration" (of B in L_1 or of A in L_2). If and as long as the curves aK and bK , originating at a and b , follow the directions of the straight lines aC and bC respectively, then the ratio A/B remains unchanged in the conjugate liquids, and C may be said on this basis to have no effect. Ultimately, if the curve is closed (at point K in this case), C must be said to increase the mutual solubility, even if the curves aK and bK initially diverge as they start from the base AB, as seen in some of the isotherms of Fig. 10-16 of this section.

As long as the slopes (of aK and bK) show no effect of C, or at low concentrations of C, the ideal distribution law may be expected to hold to some degree, with respect to the concentrations of C in the two layers, the ratio c_1/c_2 remaining constant. This obviously will be probable only if the mutual solubility of A and B is very small, so that solution a is almost pure A, and b almost pure B. Many attempts have been made to establish general mathematical relations for the effect of C on the angle of the tie-lines, or on the ratio c_1/c_2 , at higher concentrations, or for the change in the conjugate compositions a' and b' ; but although empirical formulas⁹ suitable for groups of related systems are available, the general problem is not solved. Some of these empirical formulas for the tie-line distribution assume that the tie-lines have some common point of intersection if extended outside the binodal curve.¹⁰ The problem has also been attacked on the basis of the activity coefficients of C in the systems A-C and B-C separately, as derivable from azeotropic relations and other such properties.¹¹ In Fig. 10-13 there is presumably a greater degree of positive deviation (or a smaller degree of negative deviation) from Raoult's law in L_1 than in L_2 .

The complex x is a mixture of two liquids, a and b , in the ratio xb/xa . As C is added, the compositions and relative amounts of the conjugate liquids change, so that when the total composition reaches x' , the liquids are a' and b' in the ratio $x'b'/x'a'$. When the binodal curve is reached, at x'' , the last trace of L_1 disappears, leaving a single liquid phase. If the line Cx is on the left of K, the phase disappearing is L_2 . If Cx passes through K,

⁹ D. B. Hand, *J. Phys. Chem.*, **34**, 1961 (1930); A. V. Brancker, T. G. Hunter and A. W. Nash, *Anal. Chem.*, **12**, 35 (1940); I. Bachman, *ibid.*, **12**, 38 (1940); D. F. Othmer and P. E. Tobias, *Ind. Eng. Chem.*, **34**, 693 (1942); C. E. Dryden, *ibid.*, **35**, 492 (1943).

¹⁰ D. N. Tarasenkova and I. A. Paulsen, *Acta Physico-Chim. U.R.S.S.*, **11**, 75 (1939); D. N. Tarasenkova, *J. Phys. Chem., U.S.S.R.*, **14**, 589 (1940); I. Bachman, *J. Phys. Chem.*, **44**, 446 (1940).

¹¹ R. E. Treybal, *Ind. Eng. Chem.*, **36**, 875 (1944); based on J. H. Hildebrand, *Solubility of Non-Electrolytes*, Reinhold, N. Y., 1936; p. 184.

the phases become identical in composition and amounts at K, the critical solution point.

If liquid A is added to liquid u ($B + C$), a second liquid phase appears when the composition u' is reached. During further addition of A, the two phases change in composition and relative amounts, the first phase disappearing when the total composition u'' is reached. Similarly, addition of liquid B to liquid v gives a turbidity (emulsion) at v' , and a homogeneous single liquid again at v'' . By such titration with A of binary B–C liquids, that portion of the curve on the B side of the tangent from A to the curve may be plotted; similar titration with B may be used to plot the curve on the A side of the tangent from B. If the binodal curve is known then it is clear that this titration process may be used in reverse for the purpose of analysis. The composition of a binary solution of B and C such as u may be determined by titration with liquid A, at the temperature of the diagram, to the point of first appearance of a turbidity. The relative amount of A used to reach this point fixes a point on the known binodal curve, such as u' . Now the extension of the straight line Au' to the side BC gives u , the required composition.^{11a}

The tie-lines are determined by analysis of coexisting liquids. Devices for the determination of the distribution or of the tie-lines, given the curve alone, without the necessity of such analysis, are theoretically possible,¹² especially when the binodal curve and distribution are already known for a temperature, usually lower, where the 2-liquid area is large enough to include that at the temperature being investigated.¹³ Even with a single curve, as in Fig. 10–13, the relative weights of the phases a' and b' produced by a mixture x' of known total composition, may presumably be used to fix the tie-line, since the ratio of the amounts of the phases a' and b' must equal $x'b'/x'a'$.¹⁴

The device of plotting a so-called “conjugation curve,” as used by A. S. Coolidge in the *International Critical Tables*,¹⁵ is useful for the representation of the isothermal distribution and for estimating the composition of the plait point (Fig. 10–14). The known tie-lines are used to plot the

^{11a} If the original liquid is a ternary solution of known A content, this quantity of A is added to the quantity of A required in the titration, to fix the point u' on the known curve, whereupon the original ternary composition, falling on the line $u'u$, may be calculated; S. Siggia and J. G. Hanna, *Anal. Chem.*, **21**, 1086 (1919).

¹² For example: W. D. Bancroft and S. S. Hubbard, *J. Am. Chem. Soc.*, **64**, 347 (1942).

¹³ S. W. Briggs and E. W. Comings, *Ind. Eng. Chem.*, **35**, 411 (1943).

¹⁴ See, for example, D. F. Othmer and P. E. Tobias, *Ind. Eng. Chem.*, **34**, 690 (1942). For a related idea, see T. W. Evans, *Anal. Chem.*, **6**, 408 (1934); according to W. L. Miller and R. H. McPherson, *J. Phys. Chem.*, **12**, 710 (1908), even the relative volumes of the liquids may sometimes be used.

¹⁵ *International Critical Tables*, McGraw-Hill, N. Y., 1926; Vol. III, p. 398.

conjugation curve xKy . The short branch xK represents the percentage of A in L_2 against that of B in L_1 ; for the long branch Ky the percentage of A in L_1 is plotted against that of B in L_2 . Such a curve passes through the point K, and from the smooth conjugation curve and the binodal curve other tie-lines may be obtained by interpolation. To find a' , conjugate with any given L_2 solution b' , $b'z$ is drawn parallel to CA, to the conjugation curve, and za' then parallel to BC to the known binodal curve; less accu-

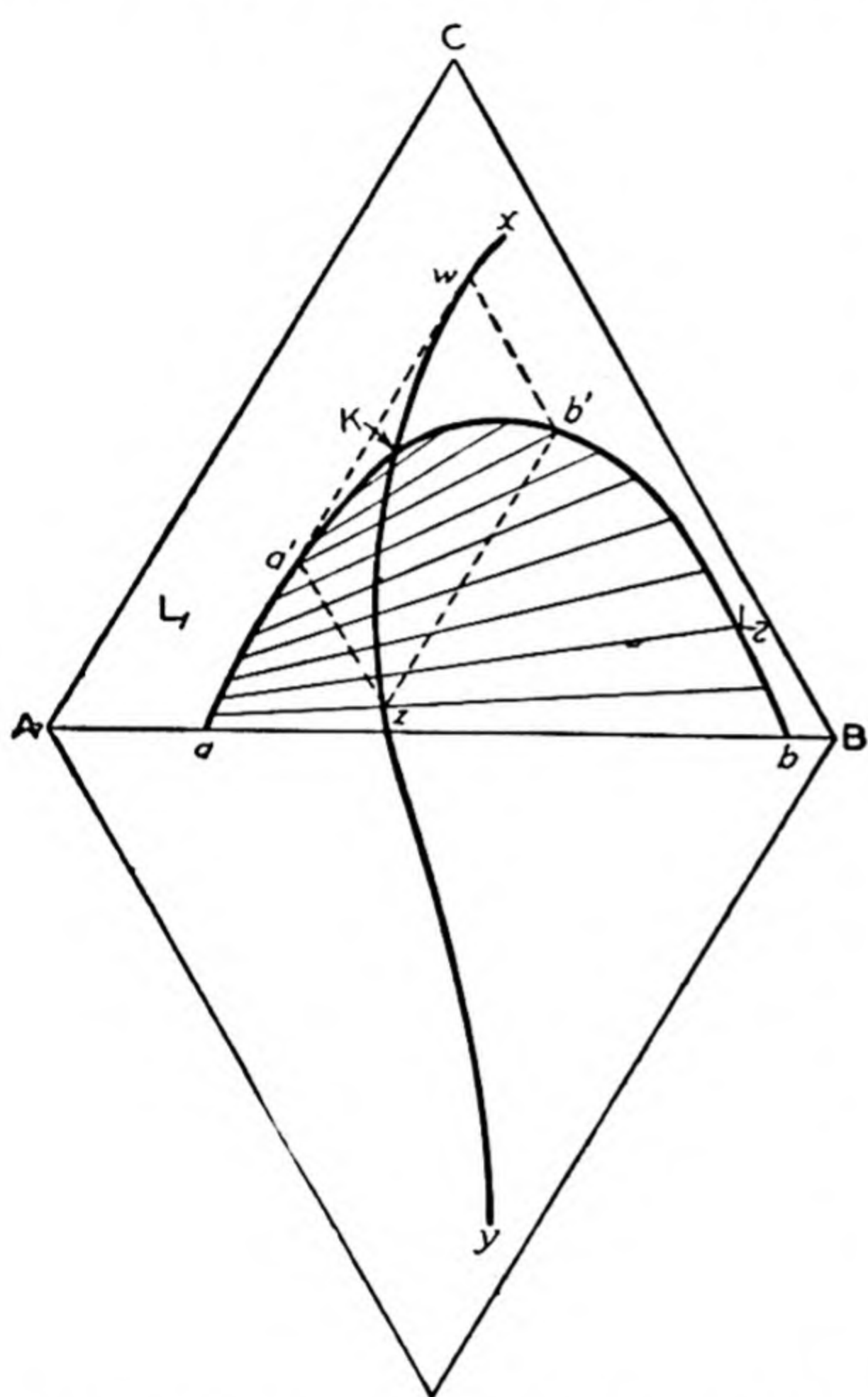


FIG. 10-14. Conjugation curve.

curve, and za' then parallel to BC to the known binodal curve; less accurately, in this case, the short branch may be used by means of the lines $b'w$ parallel to BC and then wa' parallel to CA.

If the isotherms above T_1 of Fig. 10-12 are shown together in a **polythermal projection**, such as Fig. 10-15, we note how the binodal curve vanishes to a point at K_1 . The curve KK_1 of this figure is the projection of KK_1 of Fig. 10-12, and mK_1 is the projection of points of maximum C content on the binodal curve. If, in Fig. 10-12, C first raises, instead of lowering, the upper critical solution temperature, then the *MG* in the ternary prism will be a hollow space with a dome-shaped maximum (K') and the polythermal projection, again above T_1 , will be as in Fig. 10-16. For temperatures be-

tween K_1 and K' , the binodal curve will be completely closed, with two plait points, one on the curve K_1K' , the other on $K'K$ (this curve extends to K_2 of Fig. 10-12). The line of C-maxima, mK' , becomes a line of C-minima, between K' and K_1 . The same effect, by the lowering of the lower critical solution temperature K_2 , is possible for the lower end of the *MG*. Fig. 10-16 is illustrated by the system water-phenol-acetone. K_1 , the upper consolute point for water-phenol, is at 66° , above which temperature the binodal curve is closed, vanishing entirely at 92° , the ternary maximum K' .¹⁶ Finally, the gap may exist only within the ternary system, giving a hollow, spheroidal space, with a completely closed critical curve, as

¹⁶ F. A. H. Schreinemakers, *Z. phys. Chem.*, **33**, 78 (1900). For the liquid-vapor or boiling point relations of the system with closed binodal curve, see Schreinemakers, *ibid.*, **41**, 331 (1902).

in Fig. 10-17. Now K' is the T -maximum, and K'' the T -minimum, of the MG . The outline of the gap itself is not shown; it must, however, include the projection of the closed critical curve $K'K''$.

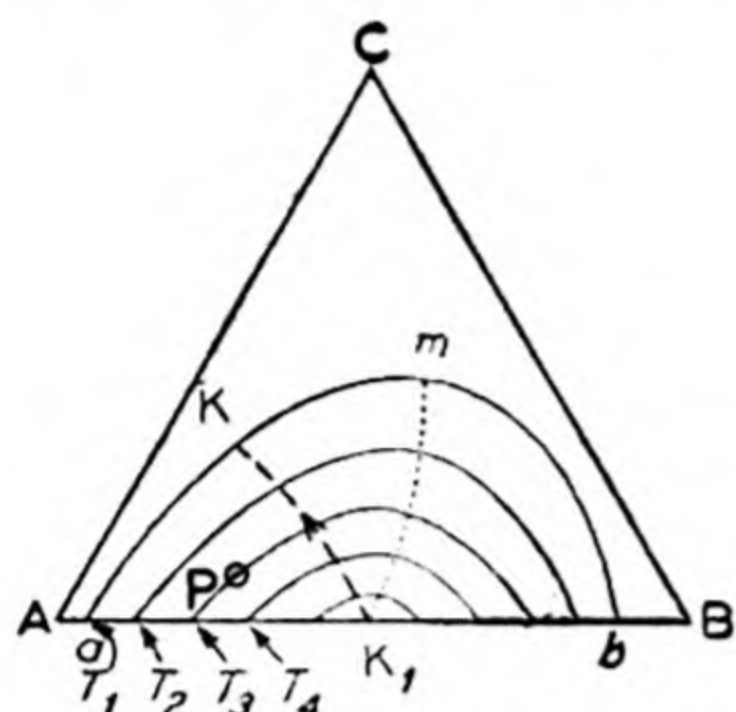


FIG. 10-15. Polythermal projection of part of Fig. 10-12.

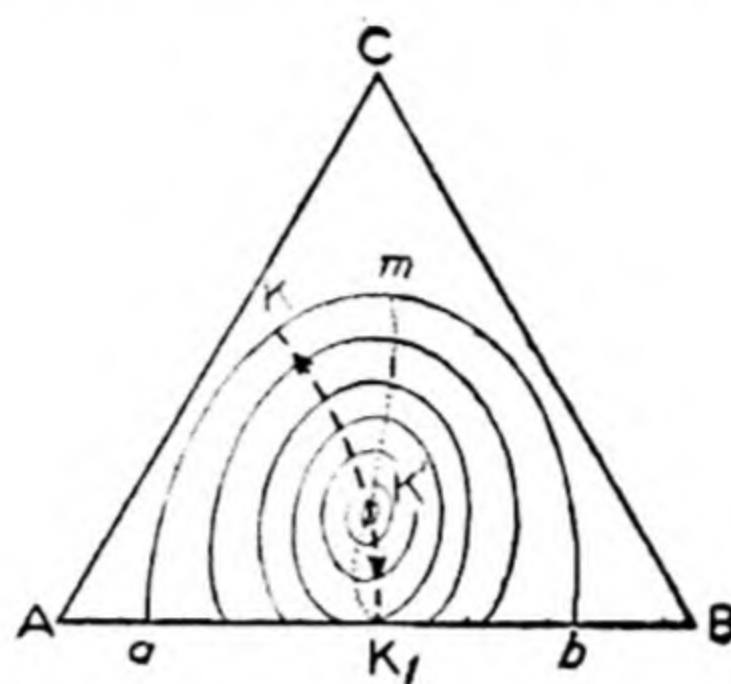


FIG. 10-16. Ternary maximum in miscibility gap.

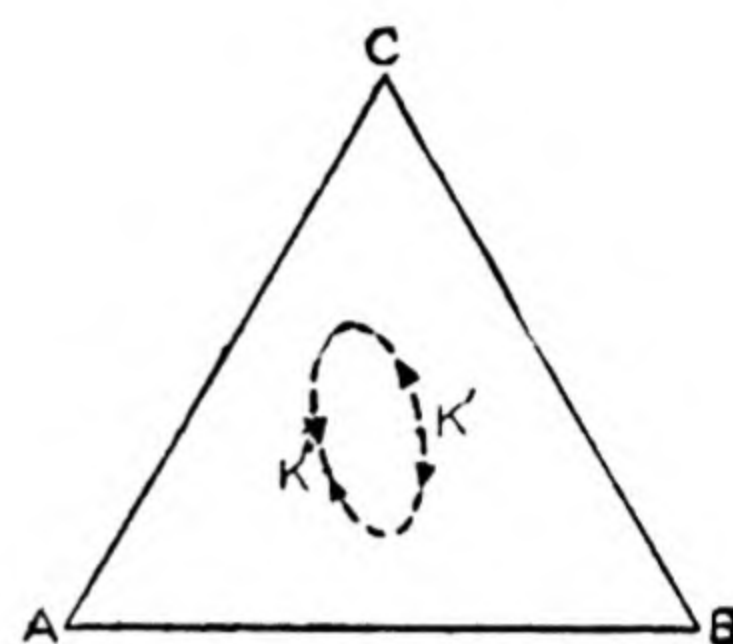


FIG. 10-17. Miscibility gap in ternary solutions only.

In these polythermal projections, which are important and useful in the representation of ternary isobaric relations, arrows on curves, as in Figs. 10-15 to 10-17, will be used to indicate the direction of falling temperature.

A liquid of composition P (Fig. 10-15) splits into two layers when cooled to T_3 , giving an infinitesimal amount of a second liquid, the composition of which is determined by a tie-line from P to the part of the binodal curve at T_3 on the B side of the critical curve KK_1 . As the temperature is lowered further, the composition and relative amounts of the two phases will vary, in accordance always with the tie-lines and the binodal curve prevailing at each temperature.

2. Miscibility Gaps in Two Binary Systems ($A-B$ and $A-C$)

At a temperature at which the two gaps do not touch, the isotherm has the appearance of Fig. 10-18(a), with two binodal curves, as in the system water-alcohol-succinic nitrile between 18.5 and 31°. ¹⁷ The plait points (K, K) normally both lie on the same side, toward A; this relation is expected since solutions of C in A or of B in A will show positive deviations compared to solutions of the system B-C, with its unlimited mutual solubility. If change of T causes an increase of the 2-liquid areas, they may finally merge by contact of their plait points, giving Fig. 10-18(b). If this process has occurred with decreasing T , the projection of the relations from the separate binary upper consolute points to the temperature of Fig. 10-18(b) is shown in Fig. 10-18(c). The point m is a minimum in the continuous critical solution curve running between the two binary upper critical solution points $K_1K'_1$, and a "saddle point" on the surface of the merged miscibility gaps.

¹⁷ F. A. H. Schreinemakers, *ibid.*, 27, 95 (1898).

In this case each (upper) binary critical solution point has been lowered by the third component. If one is raised (in A–C) and the other lowered (in A–B), the curve K'_1K_1 may rise steadily from A–C to A–B, with the relations projected in Fig. 10–18(d), as in the system water (A)–aniline (B)–phenol (C), with K_1 at 167° and K'_1 at 66° .¹⁸ Now there is a single binodal

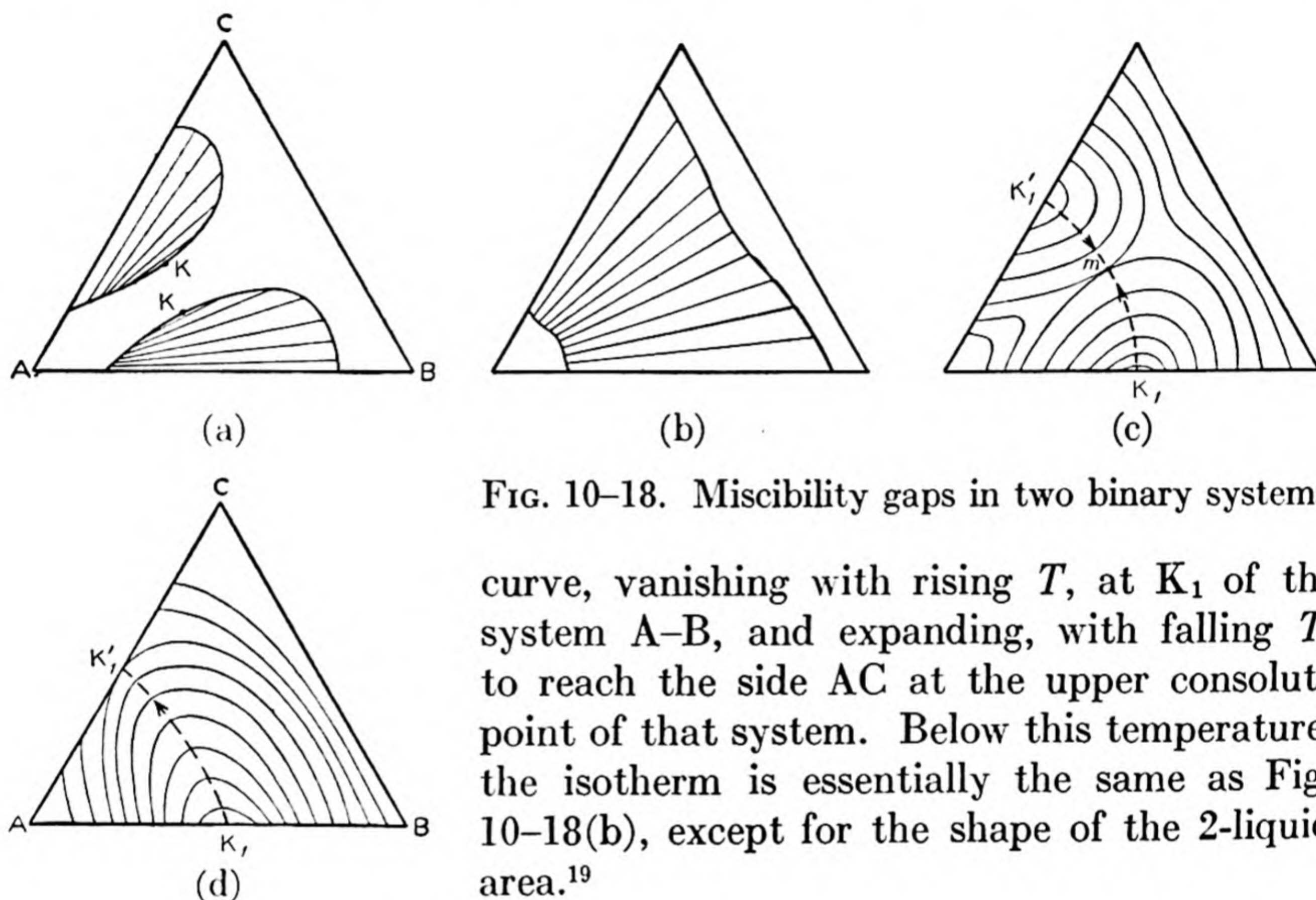


FIG. 10–18. Miscibility gaps in two binary systems.

curve, vanishing with rising T , at K_1 of the system A–B, and expanding, with falling T , to reach the side AC at the upper consolute point of that system. Below this temperature, the isotherm is essentially the same as Fig. 10–18(b), except for the shape of the 2-liquid area.¹⁹

3. Equilibria of Three Liquid Phases

With a *MG* on each of the binary systems, an equilibrium of three liquid phases becomes possible. If a third gap, on the BC side, approaches the gap of Fig. 10–18(d), either above or below the temperature of the AC consolute point, as in Fig. 10–19(a), touching it with its own critical curve (such a contact occurs at 56.5° in the system water–ether–succinic nitrile²⁰), the result is a 3-liquid system, as in Fig. 10–19(b); the three coexisting liquids are the points 1, 2, 3. The original *MG*, that is, that of Fig. 10–18(d), has been split by *MG* III, into two portions, I and II, so that Fig. 10–19(b) may be said to consist of three gaps. In 10–19(c) the penetration has proceeded further so that only a small part of gap III is still stable, and in

¹⁸ F. A. H. Schreinemakers, *ibid.*, **29**, 577 (1899); **30**, 460 (1899).

¹⁹ For the interesting case in which one binary system has an upper and one a lower consolute point, see the system water–phenol–triethylamine, studied by P. A. Meerburg, *Z. phys. Chem.*, **40**, 641 (1902).

²⁰ F. A. H. Schreinemakers, *Z. phys. Chem.*, **25**, 543 (1898).

10-19(d) the third gap is all metastable, the 3-liquid region having vanished. This 3-phase region may therefore appear and disappear (originate or be terminated) either as between 10-19(a) and 10-19(b), by the approach or separation of two miscibility gaps, or as between 10-19(c) and 10-19(d), by the emergence or submergence of one miscibility gap in another. In

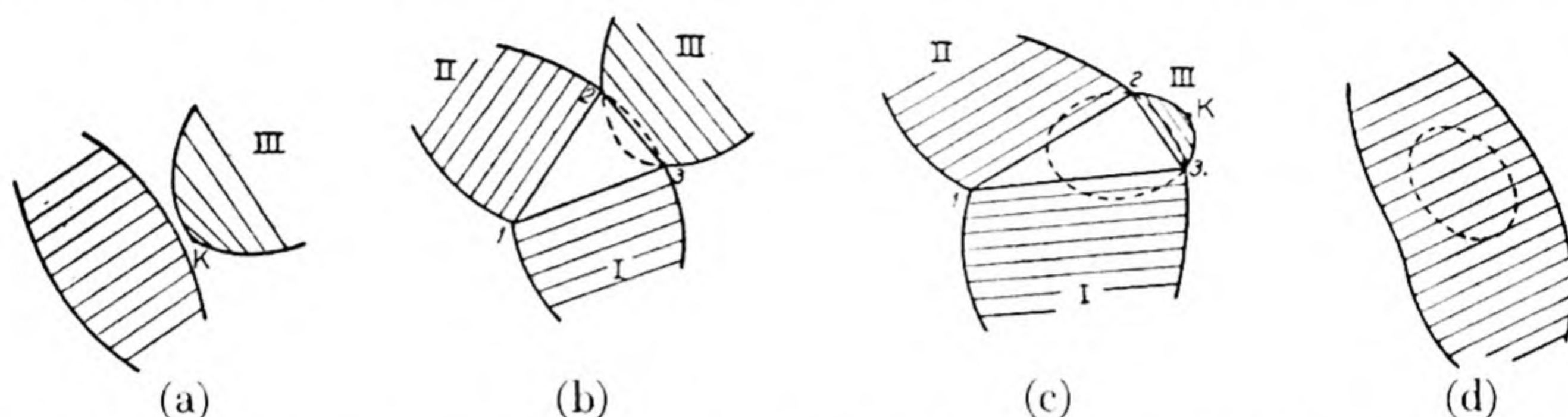


FIG. 10-19. Appearance and disappearance of 3-liquid equilibrium at singular points type k .

either case the contact of MG III, whether stable or metastable, with the other MG , is at the plait point K , which lies on its critical solution curve. The contact is therefore a singular point of type k .

Each of these gaps may extend to a side of the triangle, as in Fig. 10-20(b), or end in a plait point, as is shown for one gap, in Fig. 10-20(c). Thus, in Fig. 10-20(a) there is limited miscibility in every separate pair of components, but there is no 3-liquid system, as there is in Fig. 10-20(b).

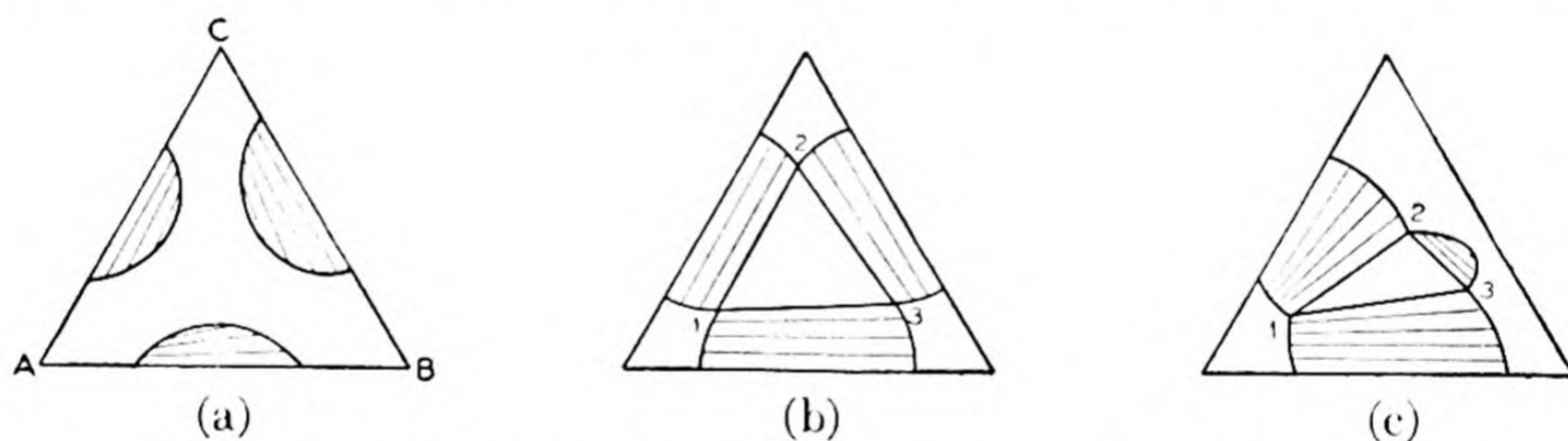


FIG. 10-20. System with three miscibility gaps.

In Fig. 10-20(c) one of the pairs has reached complete miscibility, but there is nevertheless a 3-liquid area. With further change of T , the closed gap of Fig. 10-20(c) may vanish to a point, as indicated between 10-19(c) and 10-19(d), leaving an isotherm of the type of Fig. 10-18(b). Fig. 10-20(b) is illustrated by the systems water-ether-succinic nitrile²⁰ and Fe-Zn-Pb.²¹

A ternary complex with composition falling within the triangle 1-2-3 of these figures consists at equilibrium of the three liquid phases 1, 2, and 3,

²¹ J. Timmermans, *Z. phys. Chem.*, **58**, 129 (1907).

the proportions of which would be given by the principle of center of gravity explained in connection with Fig. 10-3. The triangle represents an isobarically and isothermally invariant 3-phase equilibrium. As T is changed in the isobaric T/c prism, each of the three liquids (1, 2, and 3) of the 3-phase equilibrium of these figures undergoes a change of composition, following a 3-dimensional curve in the prism. The result is an isobaric 3-phase equilibrium represented by a space generated by the isothermal triangle 1-2-3; this equilibrium is an isobarically univariant state.

It is terminated in various ways. It may originate (or end) at an isobarically invariant point where it intersects three other such 3-phase univariant systems, involving the phases 1, 2, 3 and a fourth; such 4-phase systems will be discussed below, in section 4. In Fig. 10-19, the terminus, whether between a and b or between c and d , is a critical solution point, or a singular point of type k , at which, with rising or falling T , the liquids numbered 2 and 3, in equilibrium with liquid 1, become identical. Schematically the same relations may apply if the phases involved are three solids, if 2 and 3 are solids and phase 1 is a liquid, or if 2 and 3 are liquids (or solids) and phase 1 a vapor.

A 3-phase area may also appear (or disappear) at a singular point of type m , a non-critical terminus, for which there are two possibilities. In one case, Fig. 10-21, all the three phases involved are stable on either side

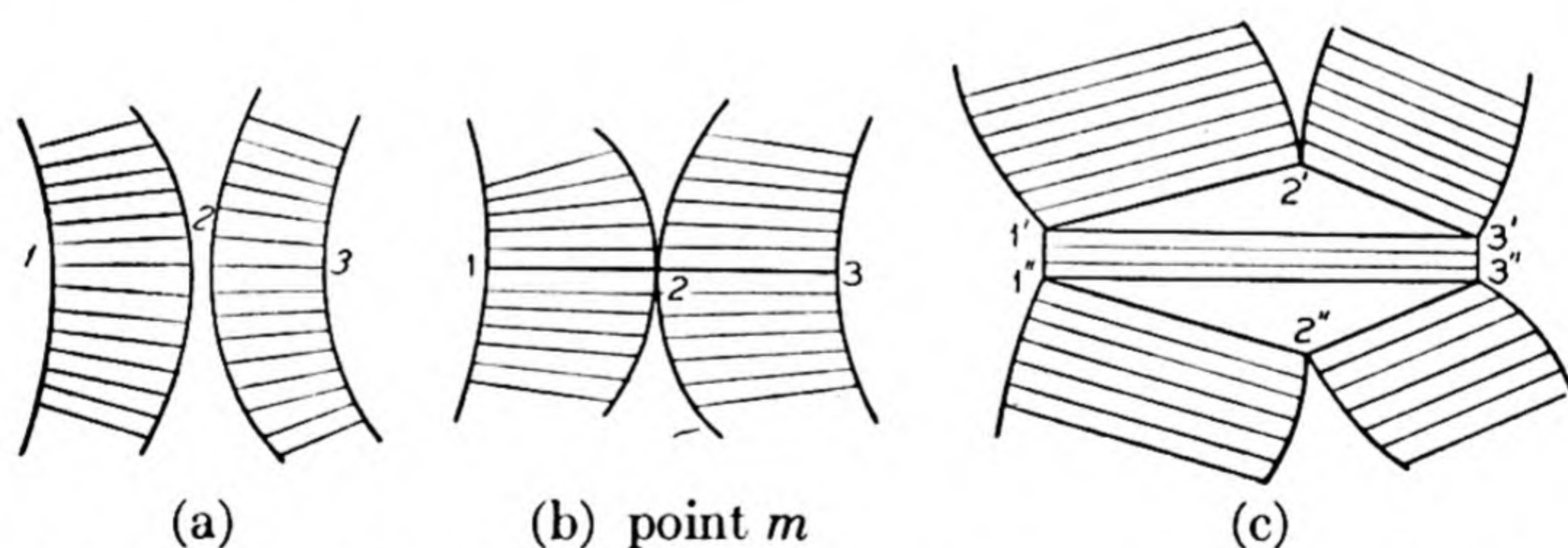


FIG. 10-21. Maximum or minimum for the equilibrium 1 + 3.

of the T (or of the P) of the singular point, and it is only a particular combination that is there terminated. In the other case, Fig. 10-22, one of the phases, of composition necessarily intermediate in respect to the other two, is stable on one side of the singular point and not at all beyond it. Plait points or critical points are not involved in these relations.

In Fig. 10-21 the two binodal curves, involving the three phases 1, 2, and 3 (which again may or may not be simply all liquids), approach each other, from the (a) side of m , so that at the T (or P) of m they have a common tie-line, 1-2-3. Beyond this point, or on the (c) side of m , the equilibrium

$1 + 3$ becomes stable, necessitating the appearance of two 3-phase equilibria, $1' + 2' + 3'$ and $1'' + 2'' + 3''$. In Fig. 10-22, the phase 2 does not exist on the (a) side of m , the only 2-phase equilibrium there being $1 + 3$. At the point m the phase 2 appears, on a tie-line of this equilibrium, giving rise then, on the (c) side, to two new 2-phase equilibria, $1 + 2$ and $2 + 3$, and also to two 3-phase regions or triangles, $1'-2'-3'$ and $1''-2''-3''$. In both cases the singular point involves a colinear 3-phase equilibrium, and represents the maximum or minimum of T (or P) for the 3-phase equilibria of Figs. 10-21(c) and 10-22(c).²²

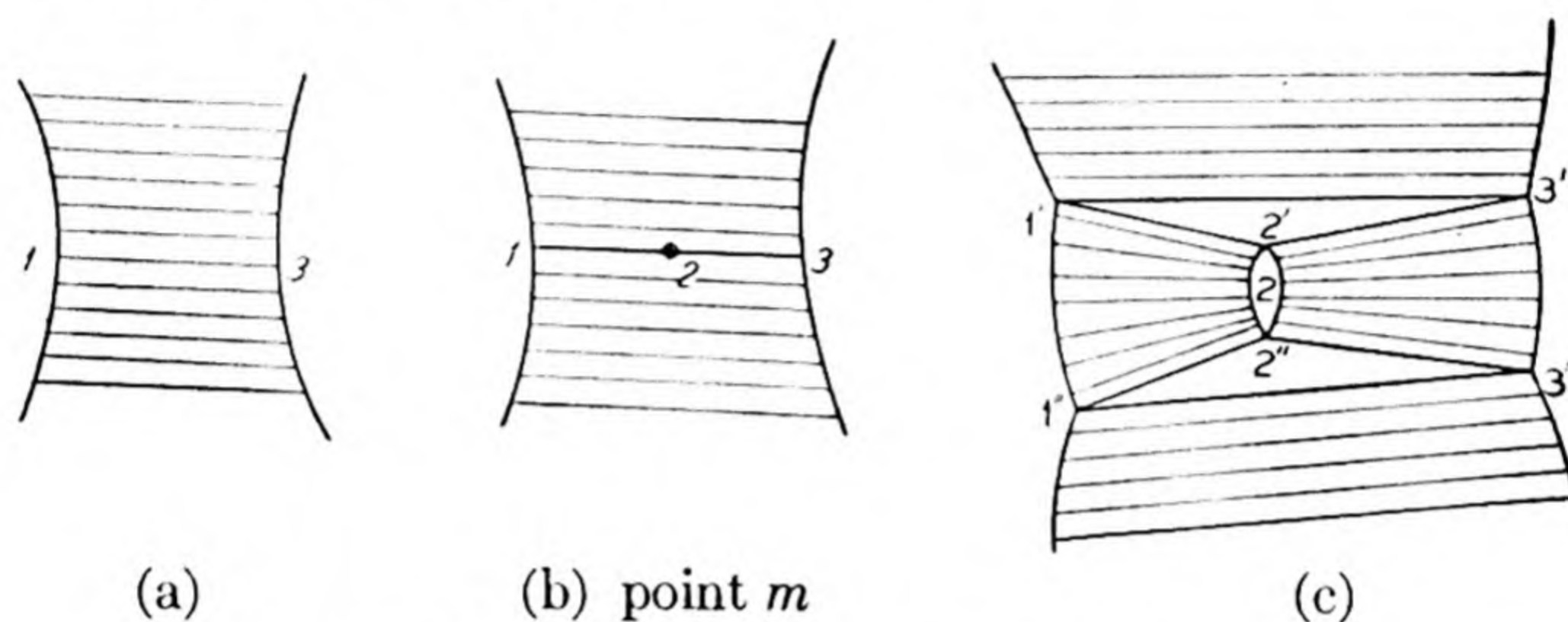


FIG. 10-22. Maximum or minimum for the phase 2.

4. *Equilibrium of Four Coexisting Liquids (or, In General, Four Condensed Phases)*

In Chapter VIII-E, it was mentioned that there could be two liquid miscibility gaps in a binary system, one on each side of the congruent melting point of a binary compound. At any rate, we may recognize the possibility of four different liquid phases in a ternary system.

At an arbitrary, constant P , four liquid phases can coexist only at an invariant T , an isothermal plane in the T/c prism, defined by the compositions of the four coexisting liquids, each having a particular, invariant composition. This (isobarically) invariant, quadruple or 4-phase plane, to be called a Q-plane, is formed by the meeting of four 3-phase triangles, and there are two ways in which four such triangles, involving four phases among them, can meet. What is here said applies to the nature of any such isobaric 4-phase invariant point of the T/c prism (and, of course, also to an isothermal invariant in the P/c prism, with P instead of T as the variable).²³

(Isobarically) Invariant System, Type A: When three of the four (isobarically) univariant equilibria approach the 4-phase system Q from one side,

²² Gibbs, Ref. H, Vol. I, 127-128; Schreinemakers, in Roozeboom (Ref. P), Vol. III, part 2, pp. 38-42.

²³ Gibbs, Ref. H, Vol. I, 122-125.

and only one from the other side, in respect to temperature change at constant P (or to pressure change at constant T), the arrangement may be called 3/1 or 1/3.²⁴ One of the four phases is stable on only one side of Q , and the 4-phase plane of Q is a triangle, with this particular phase inside the triangle. The meeting of the four triangles is then as in Fig. 10-23. On the (a) side of Q , the stable equilibria are $1 + 2 + 4$, $2 + 3 + 4$, $1 + 3 + 4$; on the (c) side, the system is $1 + 2 + 3$. If T falls from (a) to (c), the small

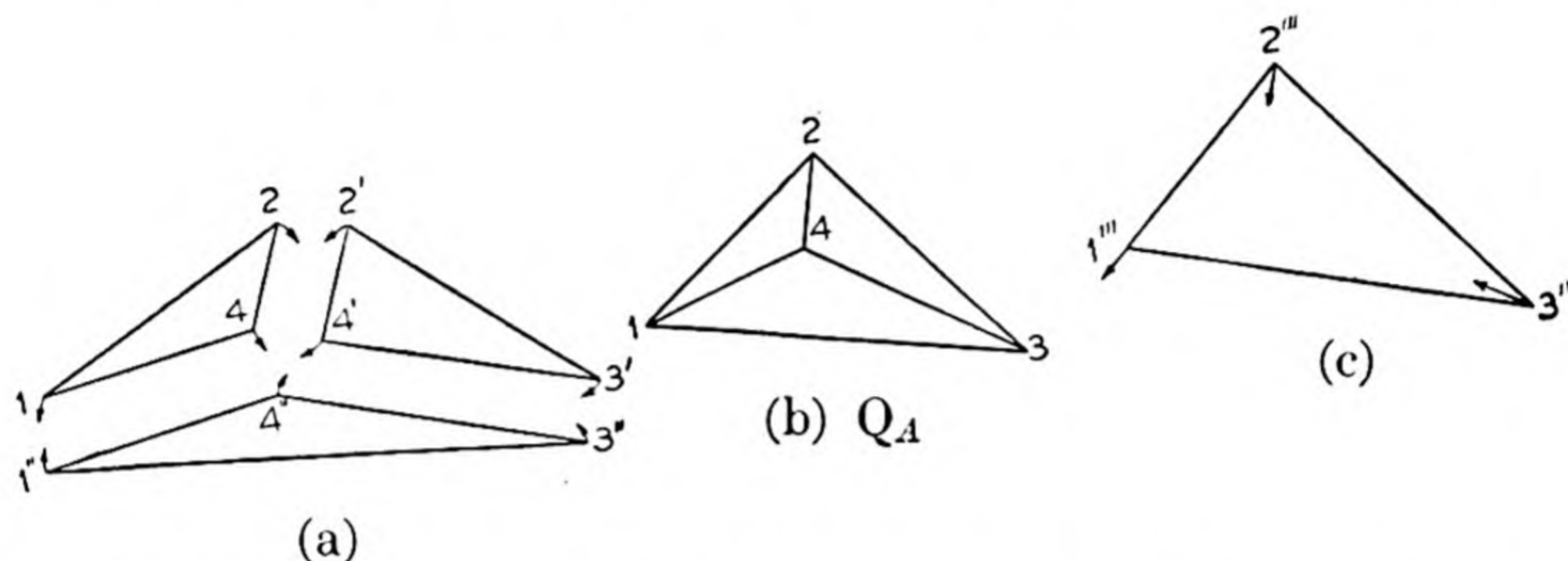


FIG. 10-23. Isobarically invariant system type A, for ternary system.

arrows indicate the change in composition of each phase (altogether twelve 3-dimensional curves here shown in "polythermal projection") with falling T . The three curves for each phase coincide at Q , which is then a triangle with phase 4, which disappears with falling T , inside the triangle.

(*Isobarically*) *Invariant System, Type B*: When two of the 3-phase (isobarically) univariant equilibria approach Q from each side of its temperature (2/2 arrangement), each phase is found on both sides of Q . Then Q is a quadrangle, as in Fig. 10-24. The stable diagonal of the 4-phase arrangement changes from 2-4 to 1-3, through Q . The combination of phases $2 + 4$ is stable only on the (a) side, the combination $1 + 3$ only on the (c) side, of Q .

An invariant point of type A (3/1 or 1/3 arrangement) may be called a **terminal invariant**, in respect to the particular phase there disappearing. It applies, for example, to a ternary eutectic, which is the temperature of disappearance (at specified P) of a liquid phase, and to the decomposition point of a compound in a ternary system, with either rising or falling T (at specified P). In general this invariant reaction may be written $4 \rightleftharpoons 1 + 2 + 3 \pm \text{cals.}$ at constant pressure. An invariant of type B (2/2) is not terminal for any phase; for the sake of a minimum of implication, we may call it a **diagonal invariant**, since it involves a shift of diagonals in respect to stability of pairs of phases. It is similar to what is called a

²⁴ See J. S. Marsh, Ref. K, *Principles of Phase Diagrams*, McGraw-Hill, N. Y., 1935, for an elaborate nomenclature.

metathetical phase reaction, or a heterogeneous double decomposition: $2 + 4 \rightleftharpoons 1 + 3 \pm \text{cals.}$, at constant P (or \pm volume at constant T). But the system is, in the present case, an "additive" one, in which at most one might expect a "replacement reaction" chemically if binary compounds are

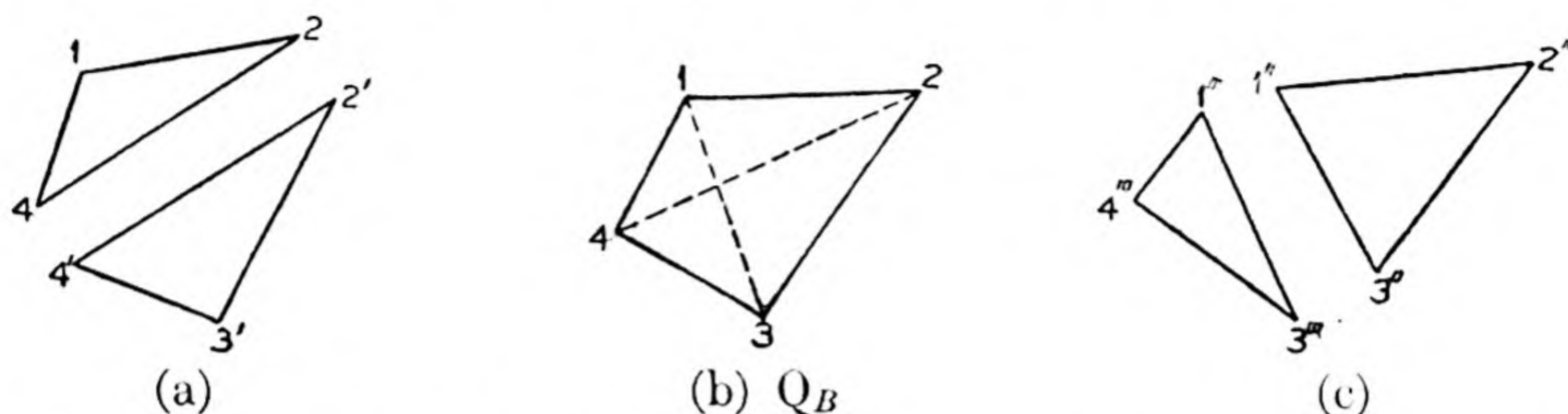


FIG. 10-24. Isobarically invariant system type B , for ternary system.

assumed to be involved: $A + BC \rightleftharpoons AB + C \pm \text{cals.}$ We shall meet with the diagonal type of invariant, however, whether or not we have reason to infer such chemical reaction in the system, that is, even when the phase diagram, involving solid solution, gives no evidence of compound formation. Later, in ternary systems called "metathetical" because of the formulas of the phases involved, it may be an interesting conjecture, then, to wonder how far it may be possible even in those cases to represent the reactions as either additive reactions or replacements.²⁵

The phases and phase pairs involved in any of the triangles, in either type of invariant system, may be related as conjugate solutions of a MG , as phases in different states undergoing phase transition, or as polymorphic forms of the same substance (component or compound). In any case, the 4-phase invariant "point" (isobaric or isothermal) of a ternary system is the intersection of four 3-phase equilibria, and of no less than twelve curves, three for each point of the Q -plane. If any of the four phases have fixed compositions (pure solids), the relations are much simplified. The conditions for the possible and impossible conjunctions of the three curves of each phase have been studied,²⁶ but, since they are not easily reduced to a brief rule, only slight reference will be made on occasion to the question.

With this general explanation, then, which applies to all kinds of 4-phase invariant points (at specified P or T), we may simply point out the two types of 4-liquid systems possible. In type A (Fig. 10-25), the phases of the 3-liquid systems are labeled to coincide with Fig. 10-23. The central liquid phase 4 ($4'$, $4''$) is stable only on the (a) side of Q_A , and the only stable

²⁵ This discussion applies to the ternary system at constant P or constant T . For the more general problem of the configuration of the five phases of a ternary quintuple point, the reader is referred to F. A. H. Schreinemakers (Ref. P), Vol. III, Part 1.

²⁶ See R. Vogel (Ref. V), pp. 612-648.

equilibrium (3-phase) on the (c) side is the 3-liquid system $1''' + 2''' + 3'''$. The invariant is terminal for liquid 4. In type *B* (Fig. 10-26), the stable arrangement changes from $1 + 2 + 4$ and $2 + 3 + 4$ to $1 + 2 + 3$ and

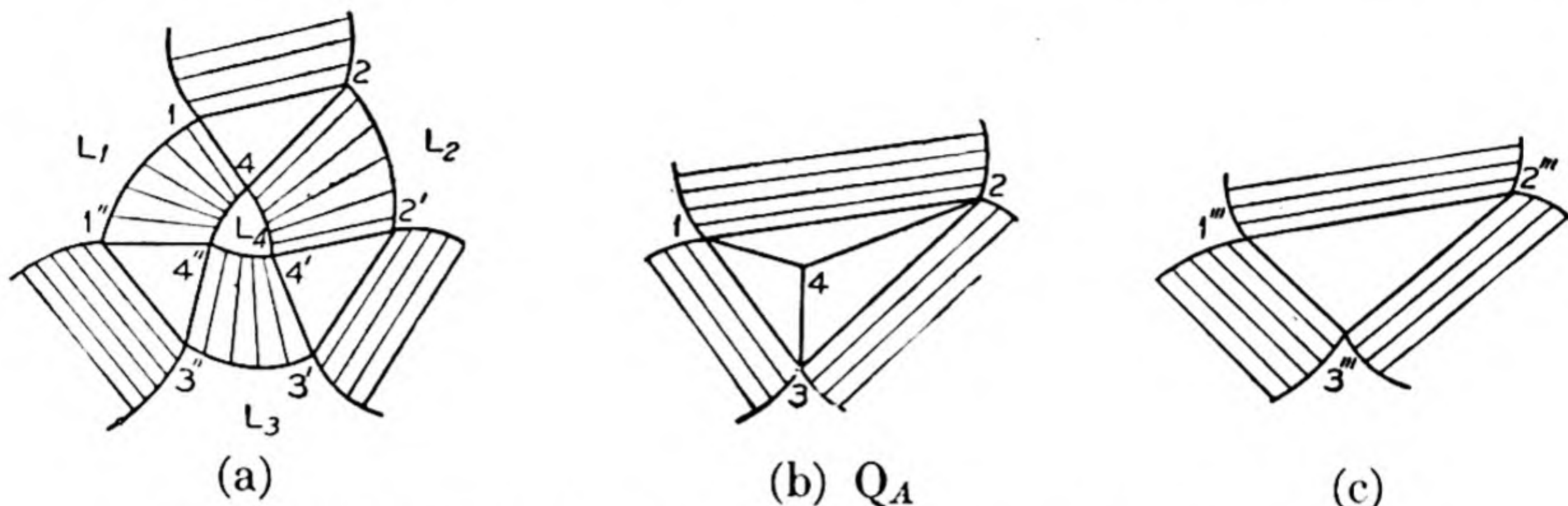


FIG. 10-25. The 4-liquid invariant Q_A , terminal for liquid 4.

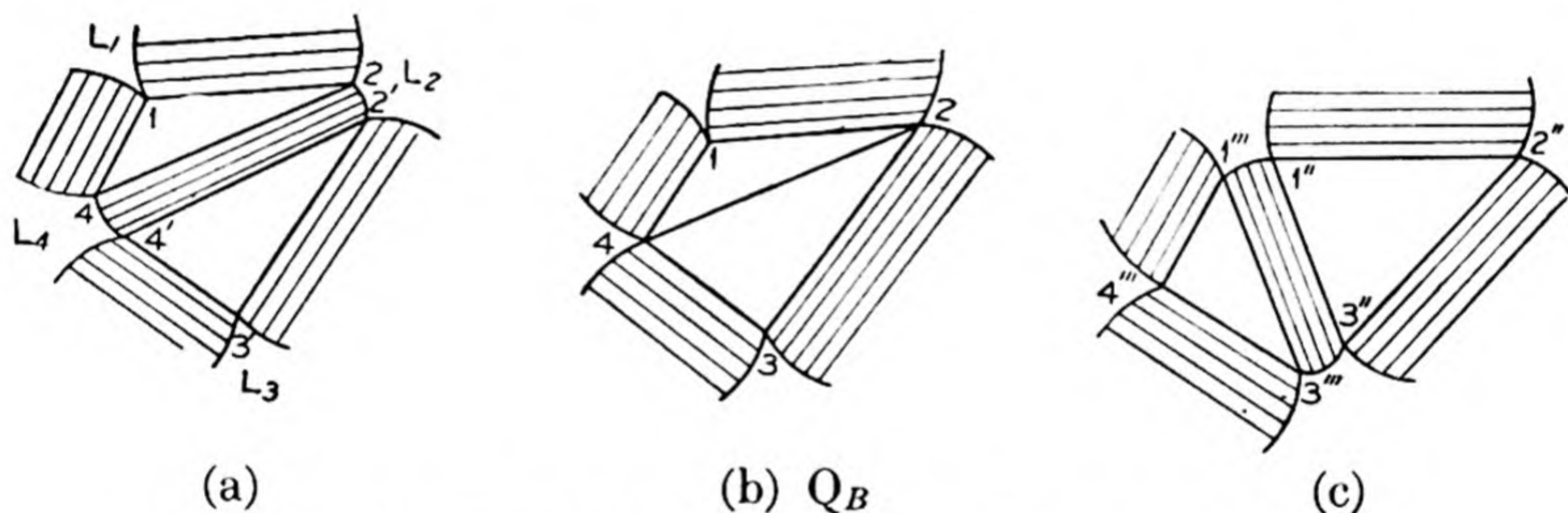


FIG. 10-26. The diagonal invariant Q_B for four liquids.

$1 + 3 + 4$, through Q ; liquids 2 and 4 can coexist as conjugate liquids only on the (a) side, liquids 1 and 3 only on the (c) side, of the diagonal invariant Q_B .

D. Univariant or Isobarically Invariant Equilibrium States

The isobarically (as also the condensed) invariant equilibrium of a system of any order is one in which $F = \alpha - \beta + 1 = 0$, or $\beta = \alpha + 1$. In a binary system this 3-phase condensed invariant is an isothermal tie-line on a T/c plane. The line is the meeting of three 2-phase condensed univariant equilibria. If the composition of the phases involved in the invariant equilibrium changes in the order in which the phases are numbered, 1-2-3, then this invariant is always terminal with respect to phase 2, since the total composition of the system must be accountable between the values 1 and 3 on either side of the invariant. The univariant equilibria must be $1 + 2$ and $2 + 3$ on one side of the invariant, and $1 + 3$ on the other side. The terminal then is the only "type" of condensed binary invariant.

In a ternary system, we have just seen, according to Gibbs, that there are two types of condensed or isobaric invariants. In the terminal invariant, type *A*, *Q*, or the quadruple equilibrium point, is an isothermal triangle in the T/c prism, the terminal phase being inside the triangle. In the diagonal invariant, type *B*, *Q* is a quadrangle with no reëntrant angles. The invariant reaction in this case is the change of diagonal of this quadrangle (Fig. 10-24); with 1-3 as diagonal, the equilibria are $1 + 2 + 3$ and $1 + 3 + 4$ on one side of the invariant, while with 2-4 as the diagonal on the other side, the equilibria are $1 + 2 + 4$ and $2 + 3 + 4$.

In a quaternary system the isobaric or condensed invariant "point" is a 5-phase equilibrium, arising at the intersection of five 4-phase univariant equilibria. But it will easily be seen that except for the additional dimension in the coordinate system the possibilities for the invariant reaction remain the same as those in the ternary system.^{27, 28} The T/c relations now require a 4-dimensional space, but the composition relations for the condensed isothermally invariant 5-phase or quintuple point involve only three dimensions. If the invariant is terminal with respect to one of the five phases (type *A*), then *Q* is a tetrahedron (1-2-3-4) in this composition space, with the terminal phase (5) inside the tetrahedron (Fig. 10-27). On one side of the temperature of *Q*, the only univariant equilibrium is $1 + 2 + 3 + 4$, or the large tetrahedron not involving phase 5. On the other side of *Q*, the large tetrahedron splits into four sub-tetrahedra, each involving the phase 5, resulting in the four 4-phase univariant equilibria $1 + 2 + 3 + 5$, $1 + 2 + 4 + 5$, $1 + 3 + 4 + 5$, and $2 + 3 + 4 + 5$. If phase 5 is a liquid and the others solids, this would be a quaternary condensed eutectic point. In general, $5 \rightleftharpoons 1 + 2 + 3 + 4 \pm \text{cals. at constant pressure}$.

For a type *B* invariant, diagonal in reaction, *Q* is a 5-cornered hexahedron (Fig. 10-28). In this figure the point 5 must be understood to lie behind the plane 1-2-3, while point 4 lies in front of it. Now the invariant reaction is such that it is approached from one side, let us say the (a) side, by two univariant 4-phase equilibria, and from the (b) side by three such equilibria. This means that from the (a) side, the hexahedron is formed from two tetrahedra, while from the (b) side it is formed from three tetrahedra. It is therefore divided by the diagonal *plane* 1-2-3 on the (a) side, which is then displaced by the diagonal *line* 4-5 on the (b) side. It is in this sense that

²⁷ H. W. B. Roozeboom, *Z. phys. Chem.*, **15**, 145 (1894).

²⁸ It may be shown that these alternatives remain essentially unchanged for systems of still higher order, although it becomes necessary then to consider the problem in $\alpha - 1$ dimensional space for the "spatial" relations of the $\alpha + 1$ phases involved in the condensed invariant. See P. A. Beck, *J. Applied Physics*, **16**, 808 (1945).

this invariant may still be called the "diagonal" type. The equilibria on the (a) side are therefore $1 + 2 + 3 + 5$ and $1 + 2 + 3 + 4$, as in Fig. 10-29; and on the (b) side, $1 + 2 + 4 + 5$, $1 + 3 + 4 + 5$ and

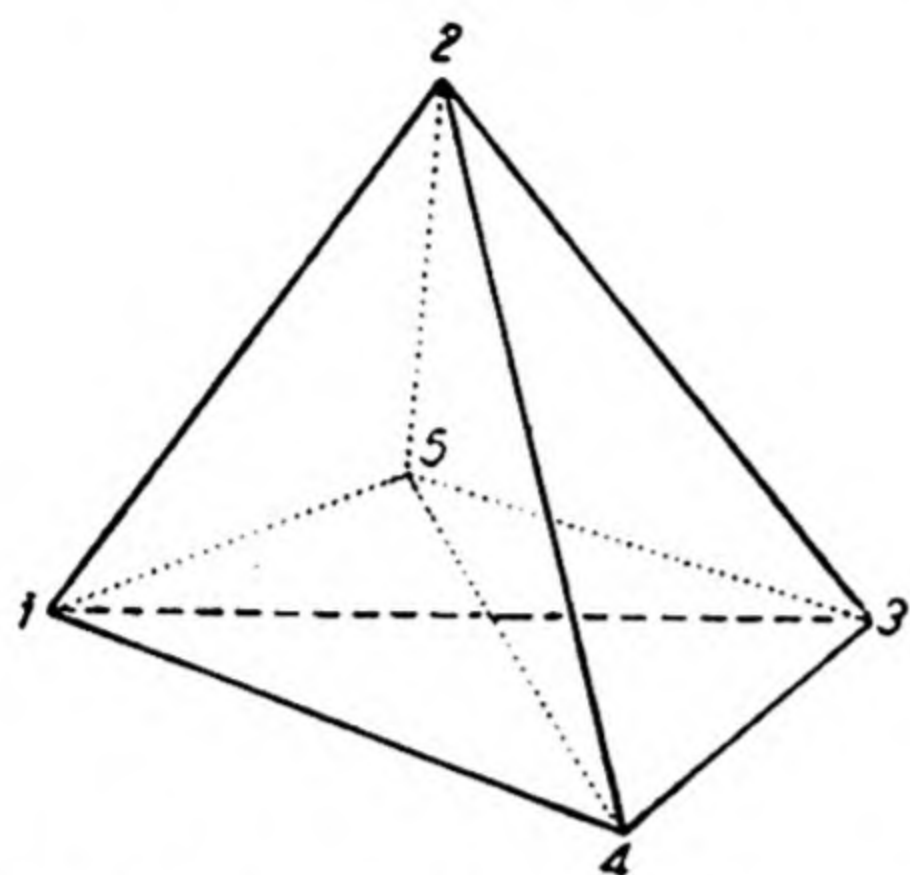


FIG. 10-27. Terminal condensed invariant, Q_A , for quaternary system.

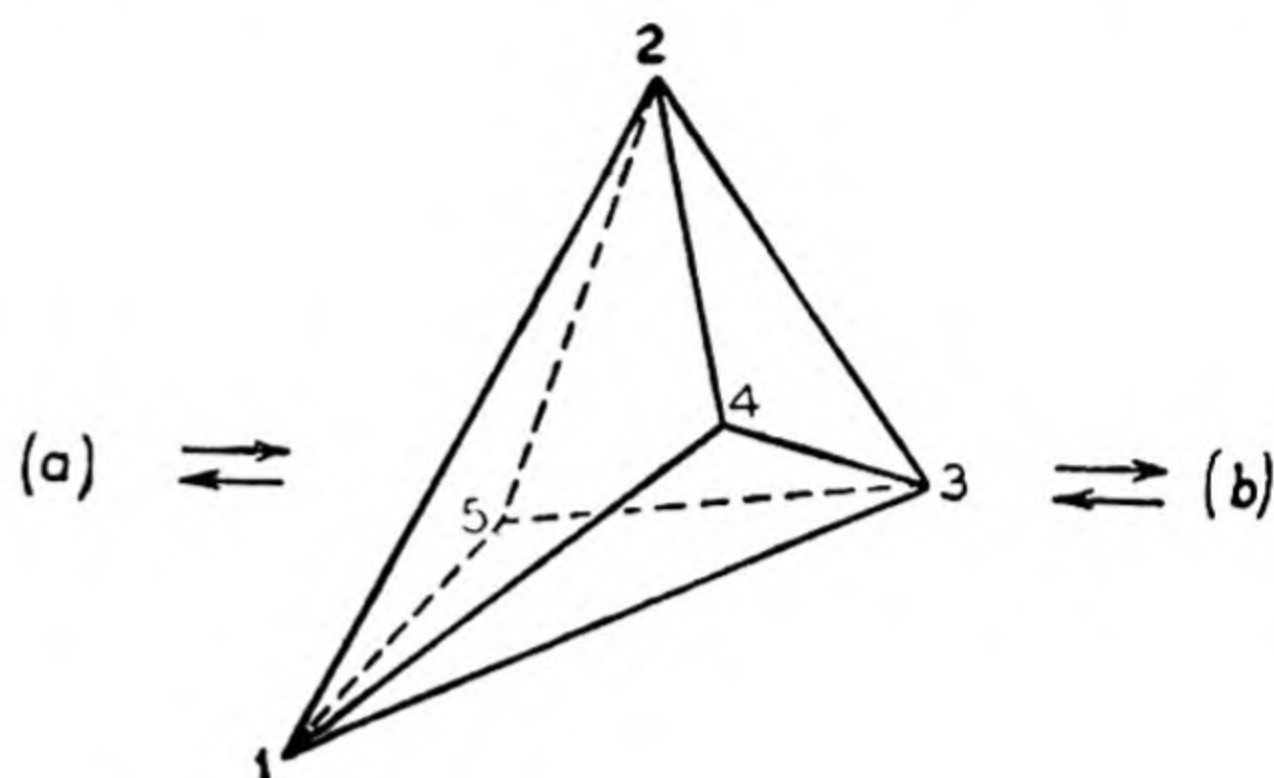


FIG. 10-28. Diagonal condensed invariant, Q_B , for quaternary system.

$2 + 3 + 4 + 5$ (Fig. 10-30). The combination of phases $4 + 5$ is not possible on the (a) side, since these phases are divided by the diagonal plane approaching from the (a) side; but all three equilibria on the (b) side involve the combination $4 + 5$ in common, since the diagonal line

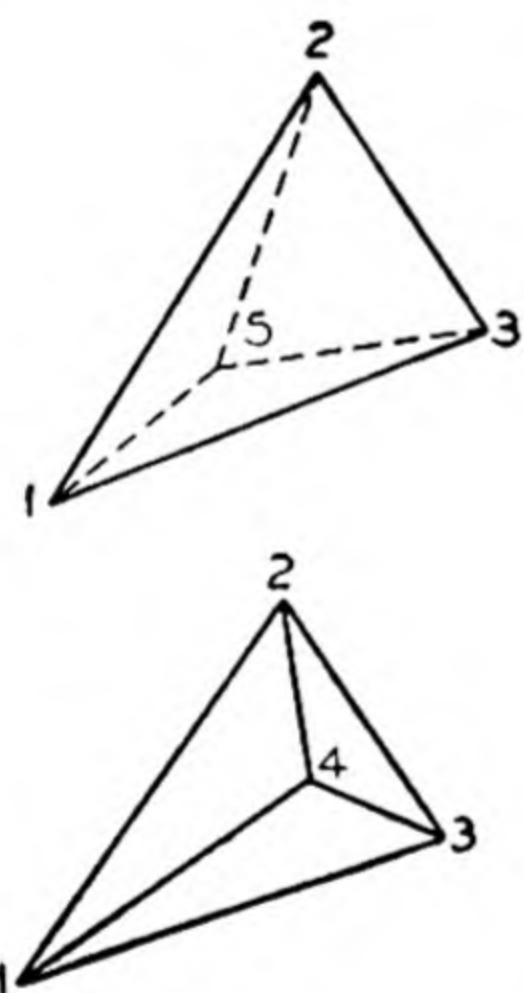


FIG. 10-29. Equilibria on the (a) side of Q_B , Fig. 10-28.

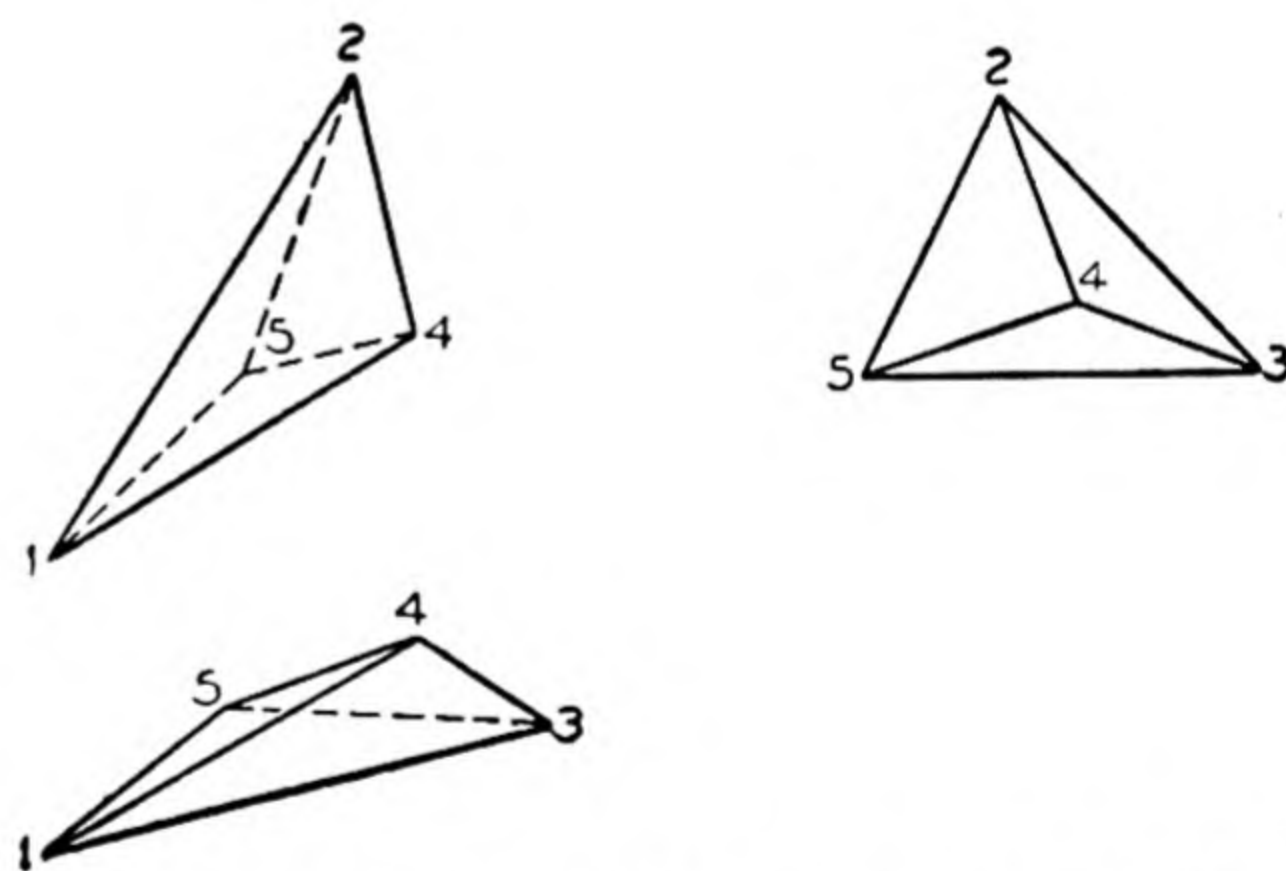


FIG. 10-30. Equilibria on the (b) side of Q_B , Fig. 10-28.

$4-5$, characteristic of the (b) side, is part of all the tetrahedra on that side. On the other hand, the combination $1 + 2 + 3$ is common to the (a) side but is excluded on the (b) side. The invariant reaction is therefore $1 + 2 + 3 \rightleftharpoons 4 + 5 \pm \text{cals. at constant pressure}$.

Chapter XI Miscibility Gaps in Phase 1

at the Phase Transition Surfaces

A. Introductory

In this chapter we shall use as the particular illustration for discussion, the miscibility gaps of solids at the melting point, assuming a single liquid phase. But again these $(T/c)_P$ diagrams apply, schematically, equally well as boiling point diagrams of ternary liquid systems of limited miscibility, and as representations of the sublimation relations; and (with the limitations mentioned in Chapter X) the same diagrams, turned upside down, give the schematic diagrams for the $(P/c)_T$ relations of the same transitions $S \rightleftharpoons L$, $L \rightleftharpoons V$, $S \rightleftharpoons V$.

A miscibility gap at the melting point curve of a binary system (A–B, specifically) leads to a break in the isobaric melting point curve, the liquid at the break being a liquid of “twofold saturation,” or one in equilibrium with two solids. If the third component C is dissolved in this liquid, then whether or not the two solids take up the component C, the binary break is the origin of a ternary liquid curve of twofold saturation. If the solids remain pure in respect to C, this curve falls in T as it enters the prism (except in certain special cases of compound formation, Chapter XII, Figs. 12–40, 12–41); if C is dissolved by either or both of the solids, the temperature of the curve may rise or fall.

A binary break caused by a *MG* represents a binary invariant (at constant pressure) of three colinear phases, or liquid plus two solids, a and b , for example, in the A–B system. As this 3-phase equilibrium moves into the T/c prism, the 3-phase line becomes a 3-phase isothermal triangle, the corners of which, representing the solid solutions α and β and the liquid l , generate three curves enclosing the 3-phase space. If the origin is a binary eutectic (Fig. 11–1) the liquid starts as the middle phase. If the curve enters the prism with falling T , the arrangement is that of Fig. 11–1(a), for since the liquidus surface lies above the solidus the liquid is always the leading corner of the triangle in the direction of falling T . If the curve enters the prism with rising T , the arrangement is therefore Fig. 11–1(b); the liquid leading the triangle toward the binary side AB. If the origin of the twofold saturation curve is a binary peritectic (Fig. 11–2) the liquid again leads the triangle into the prism with falling T in Fig. 11–2(a), and out toward

the binary side in Fig. 11-2(b) when the curve rises in T as it enters the prism.

These figures are **polythermal projections** of 3-dimensional curves in the T/c prism, on the composition triangle. As usual, the arrows indicate the direction of falling T on the projection of each of the three curves involved in the 3-phase equilibrium. If the tangent of the liquid curve projection, at any specified T , such as at point l of Fig. 11-1, cuts the 2-solid



FIG. 11-1. Crystallization curves of even reaction.

base $\alpha\beta$ of the triangle at that T , then the reaction on cooling the liquid, in equilibrium with its solids, at that T , is $L \rightarrow \alpha + \beta + \text{cals.}$ The crystallization of both solids on cooling the liquid is said to be *positive*. The liquid precipitates both solids on cooling, and therefore its composition moves away from each solid in the process, resulting in the net motion indicated. In Fig. 11-2 the tangent to the liquid curve projection does not cut the

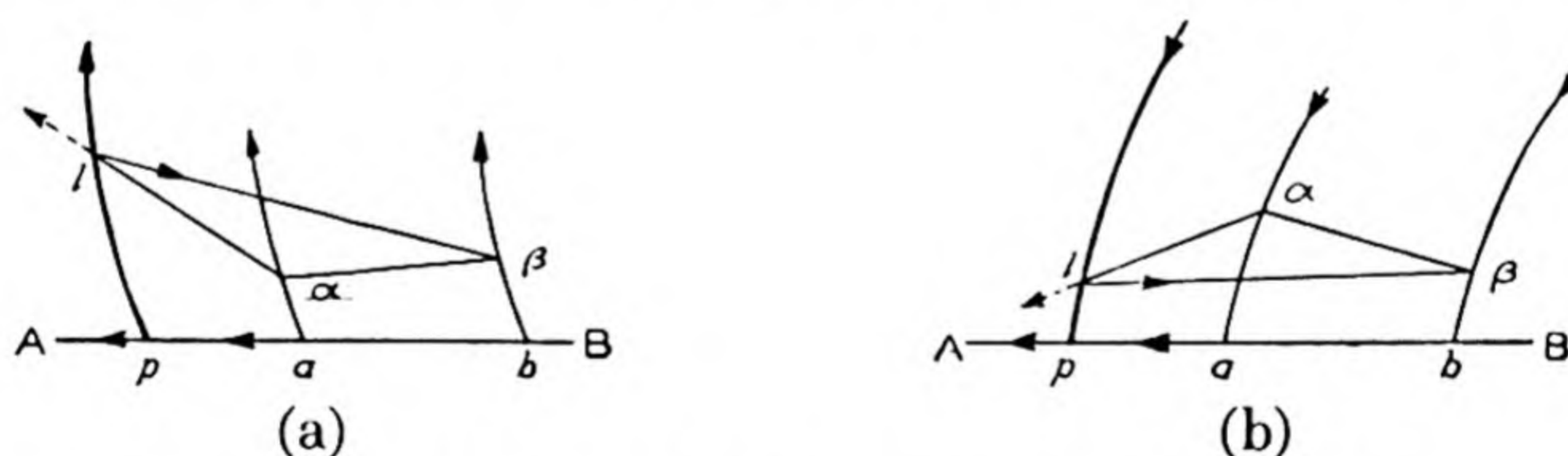


FIG. 11-2. Crystallization curves of odd reaction.

base $\alpha\beta$, and the reaction on cooling is $L + \beta \rightarrow \alpha + \text{cals.}$ It is not, of course, $L + \alpha \rightarrow \beta + \text{cals.}$, since this reaction would not satisfy the specified direction on the liquid curve. The removal of α and the dissolving of β , each process representable as a composition vector at point l (one vector away from α and one toward β), result in motion of the liquid as required by the direction of falling T ; but the removal of β and the dissolving of α would imply the opposite motion of the liquid. These considerations apply whether or not the solids are variable in composition.

We shall call the liquid curves of Fig. 11-1, **even curves**, because the crystallization of the two solids has the same sign. Those of Fig. 11-2 are therefore **odd curves**, since the crystallization of α is positive, that of β

negative, on cooling the liquid. The curve of twofold saturation originating at a binary eutectic always starts as an even curve; one from a binary peritectic, as an odd curve. But the type or sign of a curve may change, during its smooth, continuous course in the T/c prism, and such changes are possible whether or not the saturating solid phases are variable in composition. The change in type occurs when the tangent to the liquid curve projection becomes coincident with one of the liquid-solid sides of the 3-phase triangle. In Fig. 11-3(a), therefore, the curve, originating at a binary peritectic, starts as odd ($\alpha +, \beta -$), and becomes even ($\alpha +, \beta +$) at point s , when the line $s\alpha$ is tangent to the L curve. In 11-3(b), the curve, originating at the binary eutectic AeB , A and B being pure solid phases, is

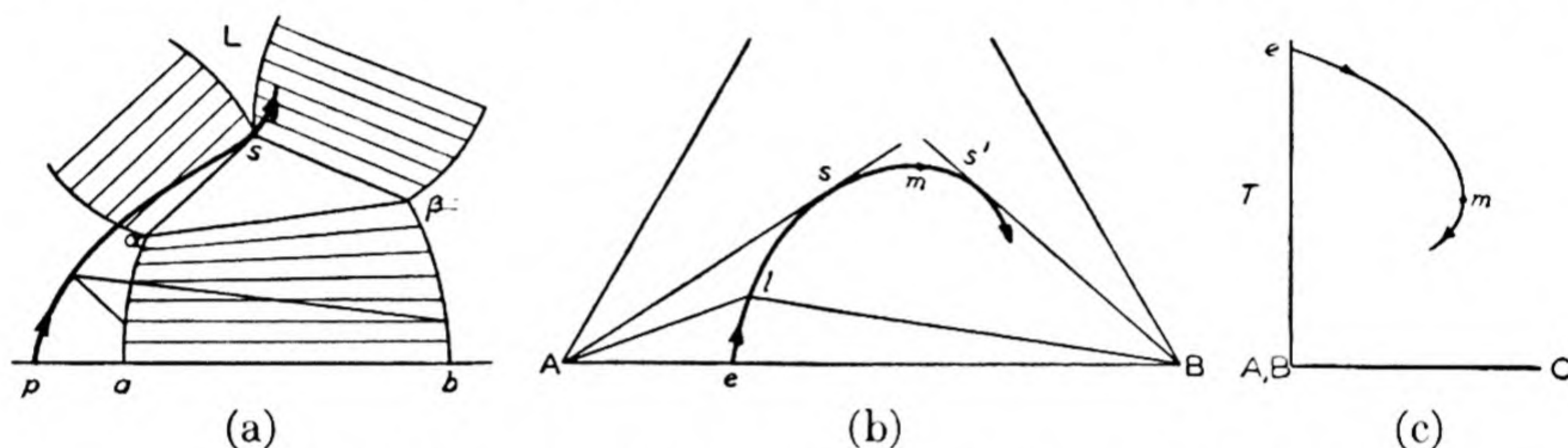


FIG. 11-3. Change of sign of the crystallization reaction.

even ($A +, B +$) from e to s , when the tangent is the line As (the side LA of the 3-phase triangle LAB). From s to s' , when the tangent goes to B , the curve is odd ($A +, B -$). Beyond s' , it is again even, but now the crystallization of both solids on cooling the liquid (in equilibrium with the solids, always) is negative ($A -, B -$). This situation arises when the curve of the liquid saturated with the two solids follows a retrograde course in respect to the side AB , as T falls, as suggested in the T/c projection of Fig. 11-3(c). The concentration of $A + B$ in the solution saturated with A and B is a maximum at the temperature of point m . The normal understanding, however, will be that the crystallization of the two solids is positive, when a curve is called "even."

If $l\alpha\beta$, in Fig. 11-4(a), is the 3-phase triangle at a particular T , then if a mixture is made up with composition P in this triangle, it consists, at equilibrium, of the three phases, l, α, β , in proportions which may be calculated as explained under Fig. 10-3. If the system is now cooled, and if equilibrium is assumed to be maintained among all three phases, the liquid moves away from point l according to the projection of the L curve as discussed under Figs. 11-1 to 11-3, and, of course, in the direction of falling T . At the same time the solid compositions α and β will follow their individual curves. Eventually, therefore, unless an invariant point is reached,

we may expect the point P to be swept by one of the sides of the moving 3-phase triangle. In Fig. 11-4(a), in which the reaction of the liquid curve is $\alpha +$, $\beta -$, the point P will be swept by the $l\alpha$ side. At that temperature the

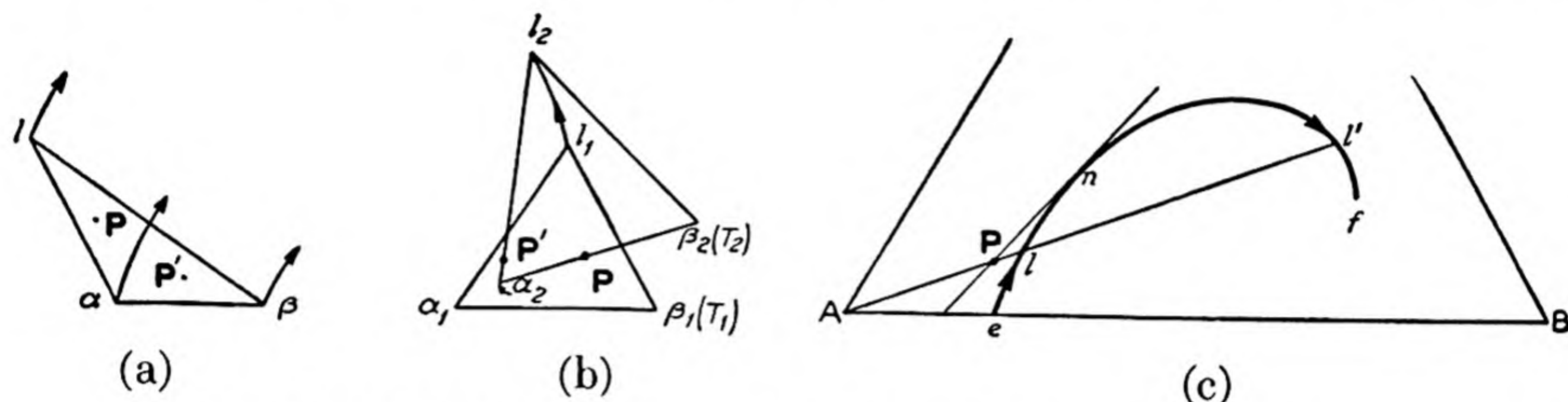


FIG. 11-4. Disappearance of a phase during crystallization.

β phase will have been consumed, and the system, now $l + \alpha$, is no longer one of twofold saturation. If the original composition is P' , the liquid will have been consumed when P' is swept by the $\alpha\beta$ side, leaving the system of two solids, $\alpha + \beta$. In 11-4(b), the same dual possibility exists even though the liquid curve is one of even reaction ($\alpha +$, $\beta +$) in the temperature range represented. If the composition is P , the liquid will have disappeared (that is, solidification will be complete) at T_2 when P lies on the side $\alpha_2\beta_2$; but if the total composition is P' , the β phase will have disappeared, leaving $l_2 + \alpha_2$, at T_2 . In Fig. 11-4(c), corresponding to Fig. 11-3(b), with pure components as solid phases, a liquid of composition P first precipitates A on cooling and eventually, with loss of A, reaches the curve ef at point l , when it becomes saturated with both A and B. P now lies on the Al side of the triangle A/B . As T falls further, and as the liquid moves on the curve, toward f , P comes to lie inside the 3-phase triangle, and the solid mixture becomes richer in B, the proportion of A to B always being given by the line through liquid and P , extended to the base AB . The ratio B/A therefore reaches a maximum when this line, Pl , becomes tangent to the curve ef , as at point n ; below the temperature of n , the proportion of B begins to decrease. The point P , still lying within the 3-phase triangle, will eventually be swept by the Al side of the triangle, when the liquid reaches the point l' . At this point B will have disappeared again, leaving $L + A$, and the liquid leaves the curve since it is now no longer saturated with two solids.

B. A Miscibility Gap Runs from One Binary System to Another

This means that the volume representing ternary solid is divided into two separate parts, at the melting point surfaces. If the gap runs from the A-B to the B-C system, one solid solution (α phase) includes the binary solid

solution of the system A–C (continuous), the other (β phase) includes the corner B.

1. The MG Is Eutectic at Both Binary Ends

There is a continuous 3-phase system, $\alpha l \beta$, now, running from the AB eutectic e to the BC eutectic e' . If T drops continuously from e' to e , as in Fig. 11-5, the projection of this 3-phase system appears as in Fig. 11-6.

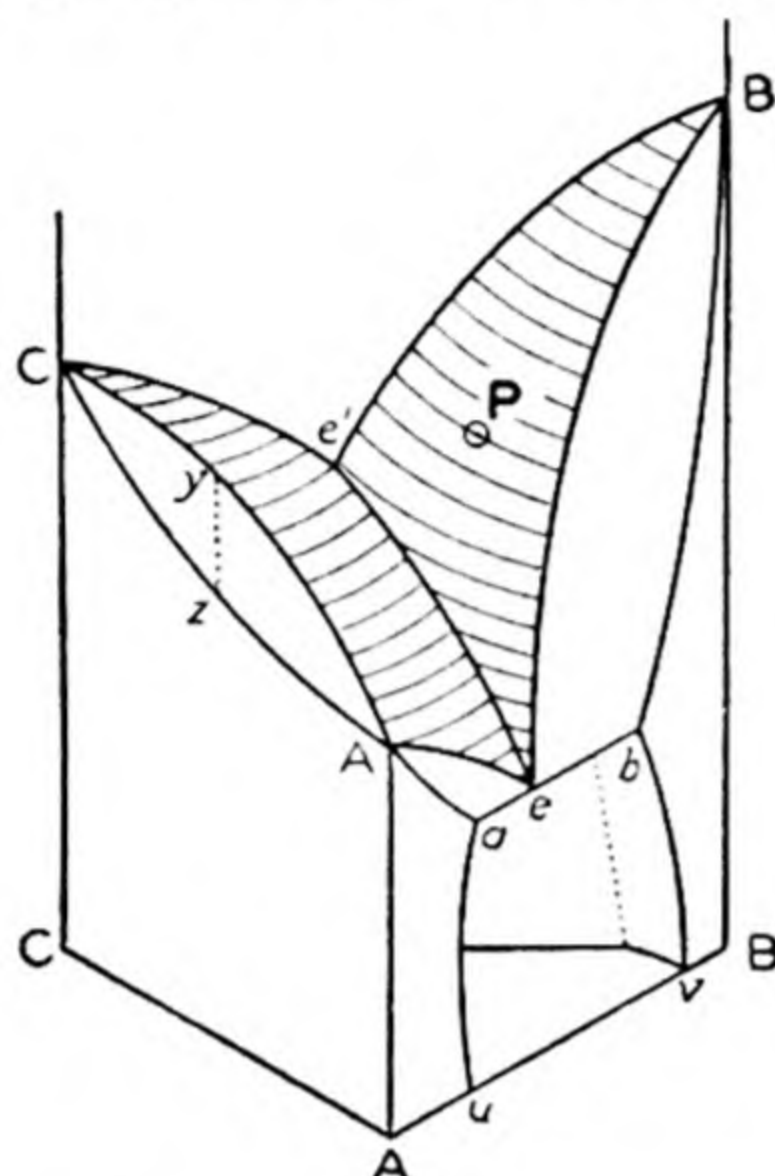


FIG. 11-5. Miscibility gap between two binary systems (both eutectic); T/c prism, with T as vertical coordinate.

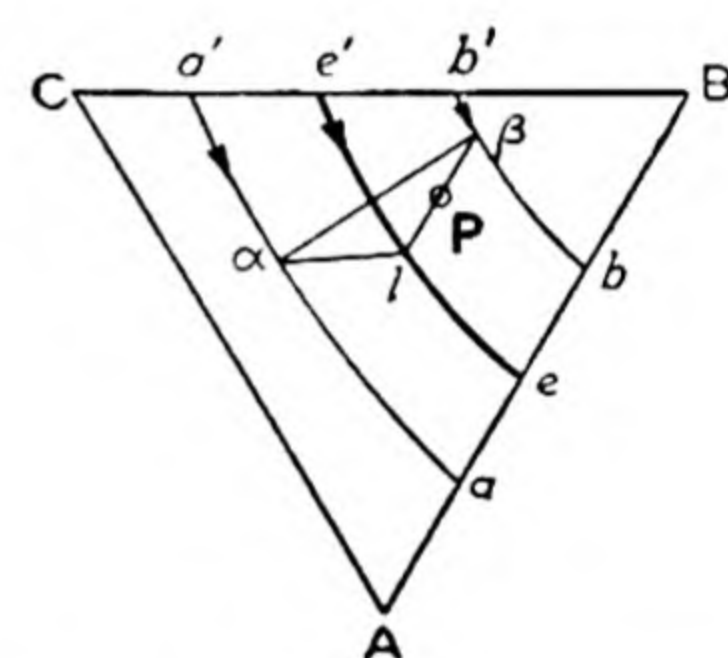
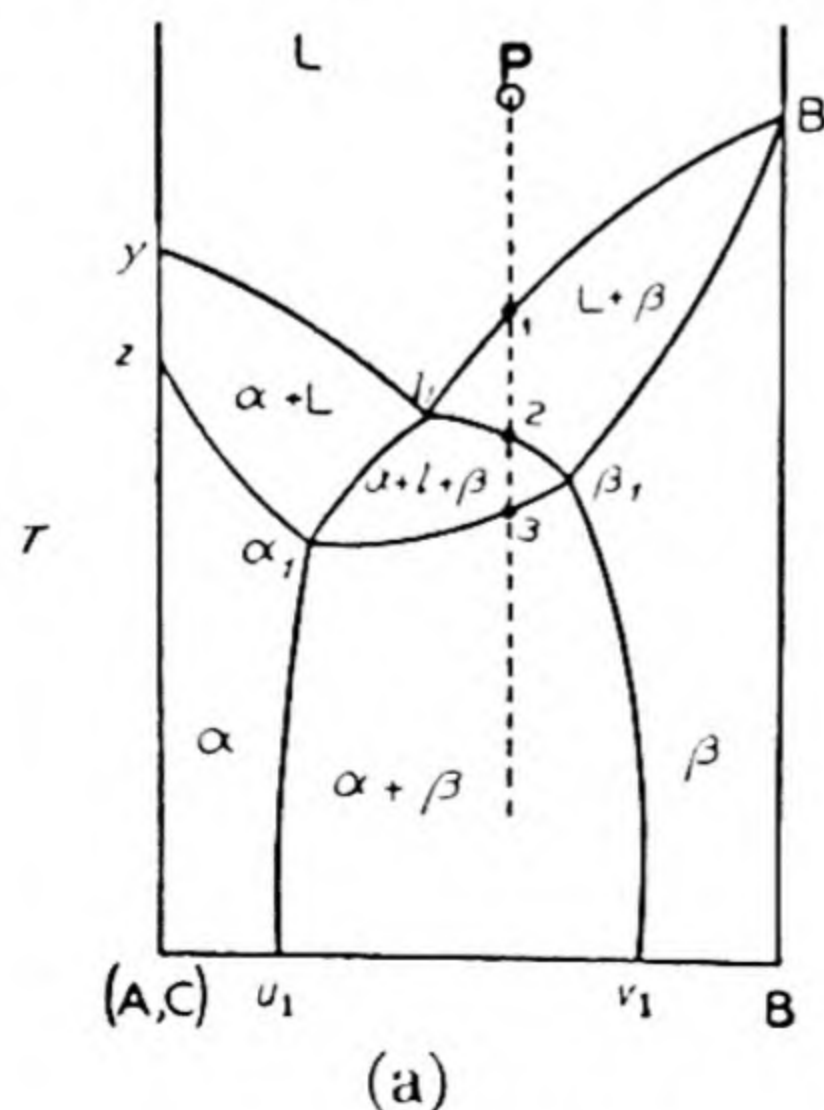
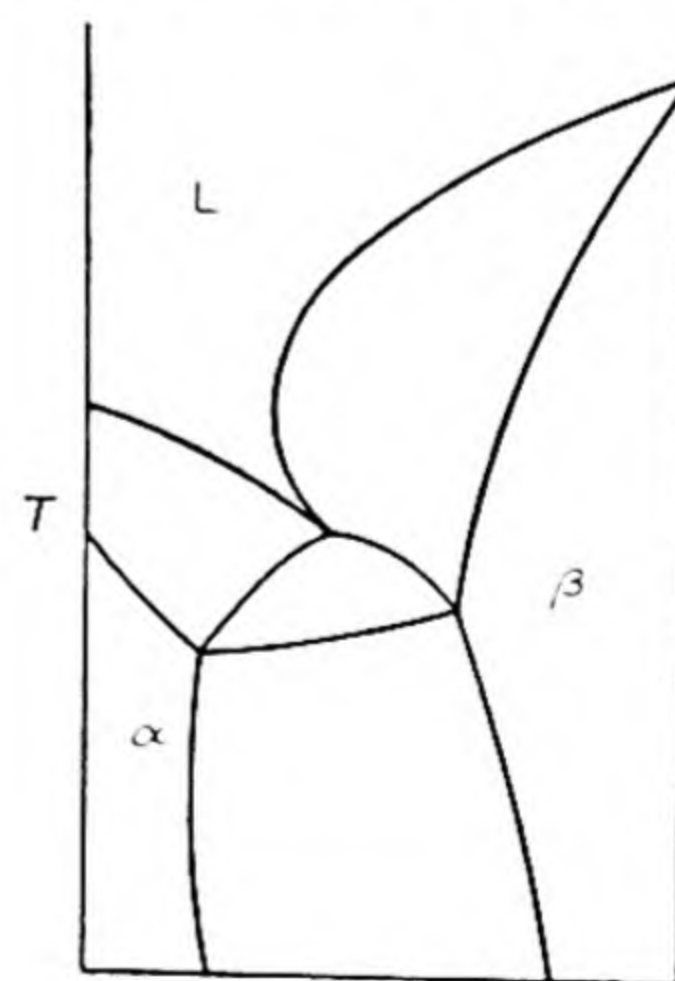


FIG. 11-6. Polythermal projection of Fig. 11-5.

The 3-phase triangle $\alpha l \beta$ proceeds, with falling T , from the BC eutectic tie-line $a'e'b'$ to the AB eutectic aeb , the liquid corner preceding the base $\alpha\beta$. The triangle is, of course, isothermal, and hence the three 3-dimensional curves (α , l , β) define a 3-sided space, closed off at each end by the lines $a'e'b'$ and aeb . A vertical section from B to the AC side at yz is shown in Fig. 11-7(a), the points y and z being on the liquidus and solidus of the binary



(a)



(b)

FIG. 11-7. Vertical sections of Fig. 11-5.

system A–C, respectively. With $e' > A$ (that is, the temperature of e' higher than the melting point of A), Fig. 11–8 shows four schematic isotherms.

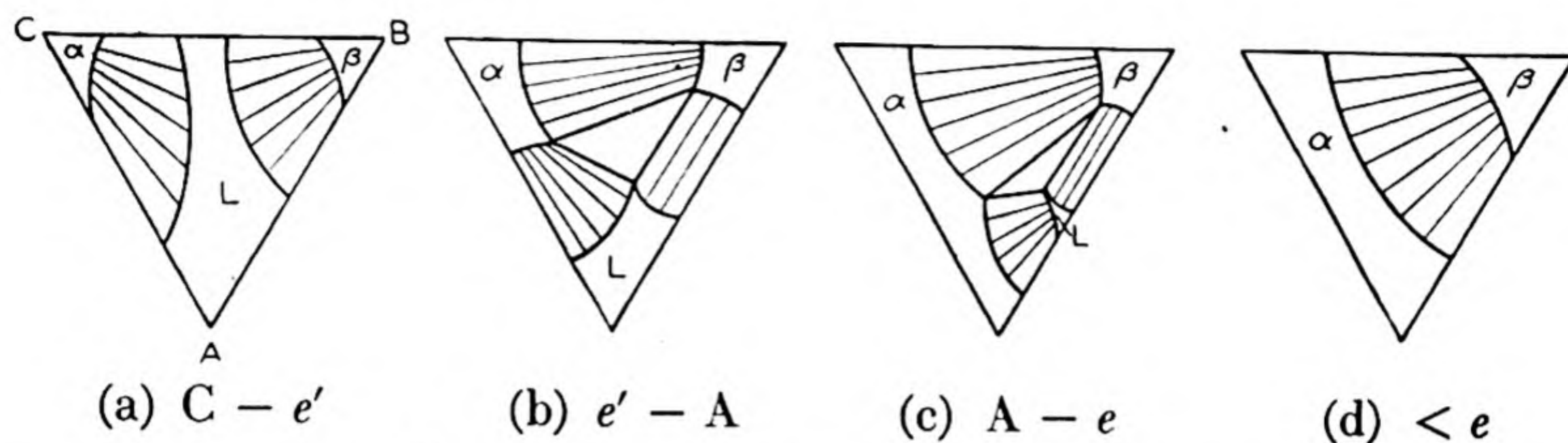


FIG. 11–8. Isotherms of Fig. 11–5.

The β liquidus surface, or the “ β liquidus” of Fig. 11–5, is projected as the area Bee' , and the corresponding β solidus, for the solid solution in equilibrium with liquid, as the area Bbb' of Fig. 11–6. Similarly the α liquidus is the area $Aee'C$ and the α solidus $Aaa'C$. This correspondence assumes, however, that the surfaces involved possess no retrograde curvature of the sort suggested in Fig. 11–7(b). With such retrograde relations the surfaces would overlap in projection, and the overlapping would not be indicated if the polythermal projection shows only the curves of twofold saturation. We shall, at any rate, always assume that the surfaces do not overlap in projection.

If, therefore, liquid with composition falling outside the MG or the area $abb'a'$ of Fig. 11–6 is cooled, it forms α or β solid solution as primary crystallization product, depending on which of the two crystallization surfaces (viewed in Fig. 11–5) it reaches on cooling; in either case the liquid is consumed before the curve ee' is reached, so that equilibria involving two solids will not arise, unless, at still lower T , the solid MG is reached. This depends on the course in the prism, of the walls of the gap, shown as the edges ua and vb on the AB side of Fig. 11–5. But phenomena occurring after solidification are of the nature already discussed in Chapter X, in connection, for example, with Fig. 10–15.

If the composition lies within the area $abb'a'$, such as point P on the B side of ee' , then the liquid and solid (β) in equilibrium during primary crystallization, reach respectively, on cooling, the curves ee' and bb' simultaneously. At this point (a second temperature break but not a constant halt), the α phase also begins to form. Both α and β now form at the expense of the liquid, all three compositions changing until all the liquid is consumed, leaving the mixture $\alpha + \beta$ when P comes to be swept by the line $\alpha\beta$ of the 3-phase triangle. If Fig. 11–7 represents the section through B and the total composition P , the successive temperature breaks occur at the points

1 for primary β crystallization, 2 when the curve ee' is reached, and 3 when the solidification is complete.

In this figure the curves yl_1 and l_1B are sections of the liquidus surfaces of Fig. 11-5, and the curves $z\alpha_1$ and β_1B are sections of the corresponding solidus surfaces. The regions marked L, α , β are single-phase homogeneous areas, and the curves α_1u_1 , β_1v_1 are sections of the walls of the solid MG . Complexes in the 2-phase regions, $\alpha + L$, $L + \beta$, $\alpha + \beta$, give phases with compositions which do not in general fall on the plane of the figure. The curves $l_1\alpha_1$, $l_1\beta_1$, and $\alpha_1\beta_1$ are not sections of the phase transition surfaces or of the MG . They are sections of the *envelopes* formed respectively by the $l\alpha$, $l\beta$, and $\alpha\beta$ tie-lines, or sides, of the 3-phase equilibrium space running from the CB eutectic to the AB eutectic. As parts of envelopes they are not, in general, straight lines. The three coexisting phases of this region are never, in general, the points l_1 , α_1 , β_1 of the section, but they vary with the total composition and the T .

The cooling process just described is one in which solid and liquid are assumed to maintain continuous equilibrium, the liquid and solid compositions being given, at any temperature, by the tie-line passing through the total composition, according to Fig. 11-8, or, in a 3-phase region, by the corners of the appropriate 3-phase triangle. The reverse process (rising T) would apply to the equilibrium melting of the solids of such a system. Parallel to this heating process would be the heating at constant pressure, equilibrium vaporization, of a ternary liquid system with the miscibility relations here assumed. Now α and β would be ternary liquid phases, and the shaded surfaces of Fig. 11-5 would represent the two parts of the vaporous surface. The T/c relations of the systems A-B and B-C would fall under Type IV of Chapter IV, Fig. 4-8(b), and the 3-phase triangle α/β of Fig. 11-6 becomes L_1vL_2 of a ternary system of two liquid layers.

These are the relations in a closed system, in which the total composition is constant during phase transition. But in distillation, or in freezing with effective removal of the solid, the boiling point or the freezing point tends toward an absolute maximum (or minimum) of the ternary liquidus. The initial composition then has significance only for the start of the process, that is, as to which of the two crystallization surfaces of Fig. 11-5 will be reached on cooling the liquid. But the residual liquid will change in composition and in freezing or boiling point according to the crystallization or boiling point paths discussed in Chapter X and shown for the present case in the following diagrams.

Fig. 11-9(a) shows the crystallization paths, and Fig. 11-9(b) the boiling point paths, for the system of Fig. 11-5; the circled points again mark the end-points, reached if the residual liquid does not completely disappear

during the actual process. In the freezing process the final residue approaches the liquid of composition e , the AB eutectic. In Fig. 11-9(b), for distillation, the lines aa' and bb' , from Fig. 11-6, are the ends of the isothermal tie-lines of two liquids (+ vapor on the curve ee'). If the original composition is that of a homogeneous phase outside this area, the phenomena are similar to those of Chapter X, and the boiling point rises to either of the two absolute maxima, the boiling point of C, for liquids in the

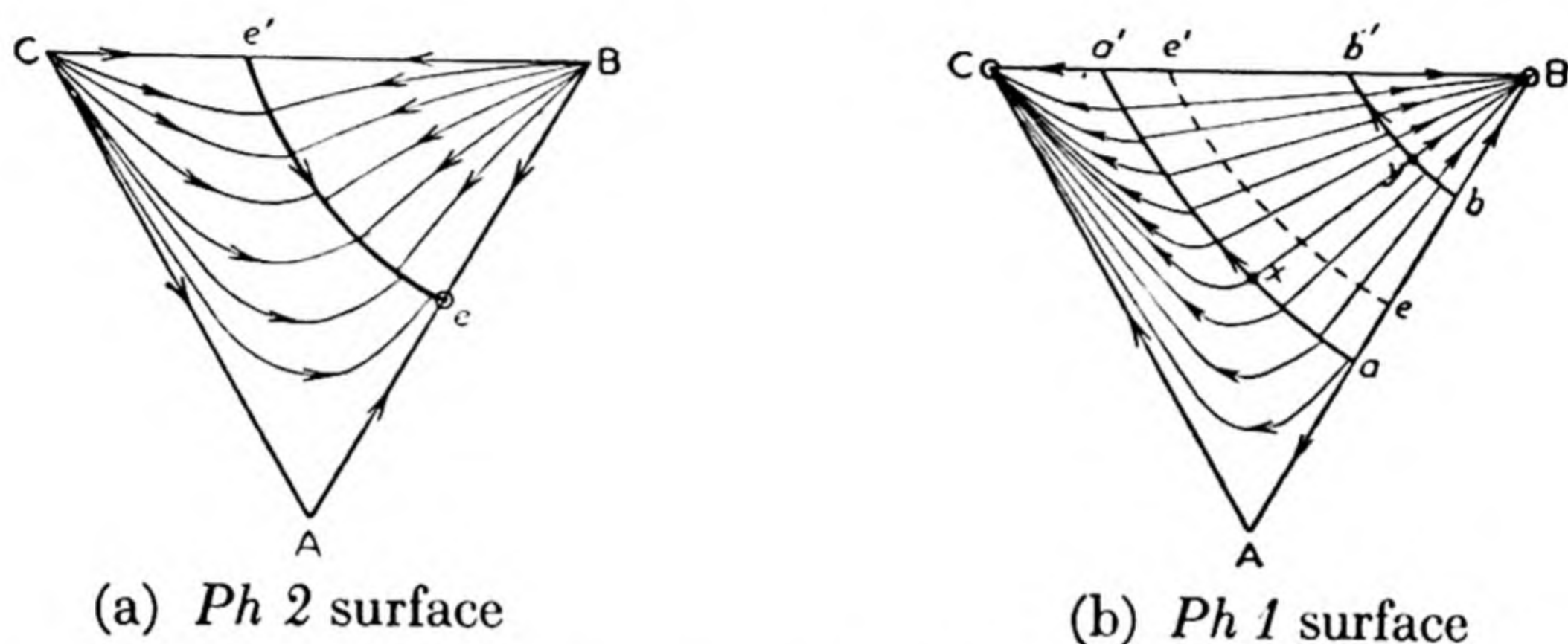


FIG. 11-9. Transition paths for the system of Fig. 11-5.

field $Aaa'C$, or the boiling point of B, for liquids in the field Bbb' (cf. Fig. 10-11(d)). For a 2-liquid system with composition anywhere on the line xy , the boiling point is that of the isothermal line xy . As the 2-liquid system boils, one of the liquids is consumed while their compositions move along the curves aa' , bb' , toward the BC side. For those on the B side of the vaporous line ee' (of "twofold saturation" here in respect to two liquid phases), the α liquid disappears, and then the β liquid leaves the curve bb' , the boiling point rising toward B. The distillation, then, of mixtures with compositions on the B side of ee' leads to pure B as the residue; the distillation of mixtures on the AC side of ee' leads to pure C as the residue.

Finally, the curve ee' of Fig. 11-5 may have either a minimum or a maximum, m , probably accompanying an "azeotropic" minimum or maximum, m_1 , in the A-C binary system. For the minimum, Fig. 11-9 becomes Fig. 11-10; an isotherm just above the minimum is shown in Fig. 11-11(a); one just below a maximum in Fig. 11-11(b), in which m is assumed $< A$. The minimum or maximum is characterized by a colinear equilibrium, a 3-phase tie-line instead of a triangle (on Fig. 11-6), and the configuration of the triangle is, of course, reversed through this tie-line; it is an isobaric, singular point, type m , as discussed under Figs. 10-21 and 10-22 in Chapter X, section C-3, and as such it is isobarically or isothermally invariant by restriction. The phases x , m , and y may be either solid $_{\alpha}$ -liquid-solid $_{\beta}$ or liquid $_{\alpha}$ -vapor-liquid $_{\beta}$. In the first case the equilibrium xmy

represents either the minimum or the maximum temperature of the 3-phase freezing point relations at constant pressure. In the second case the colinear equilibrium xmy is the 2-liquid system of either maximum or minimum

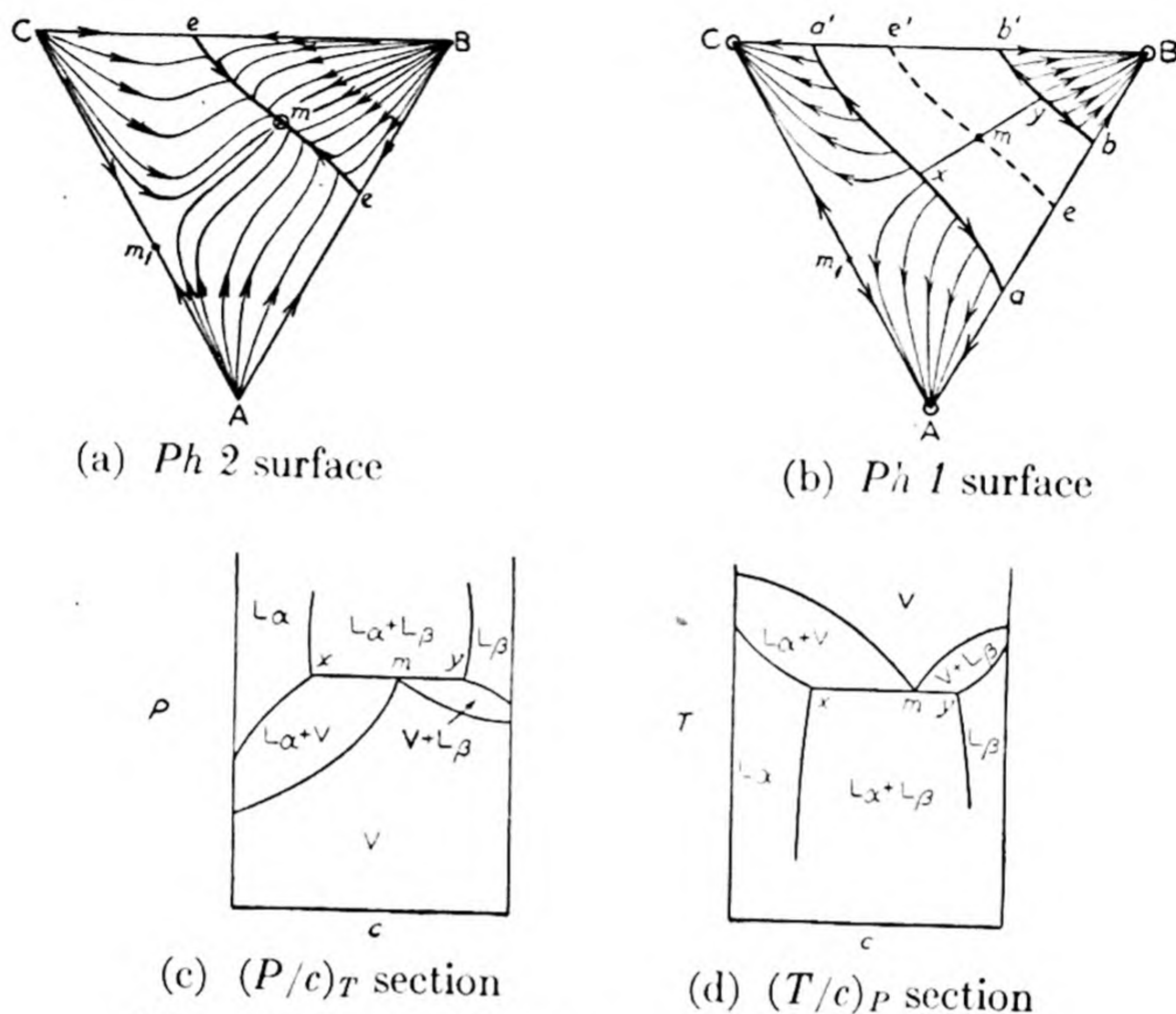


FIG. 11-10. Azotropic variation of Fig. 11-9.

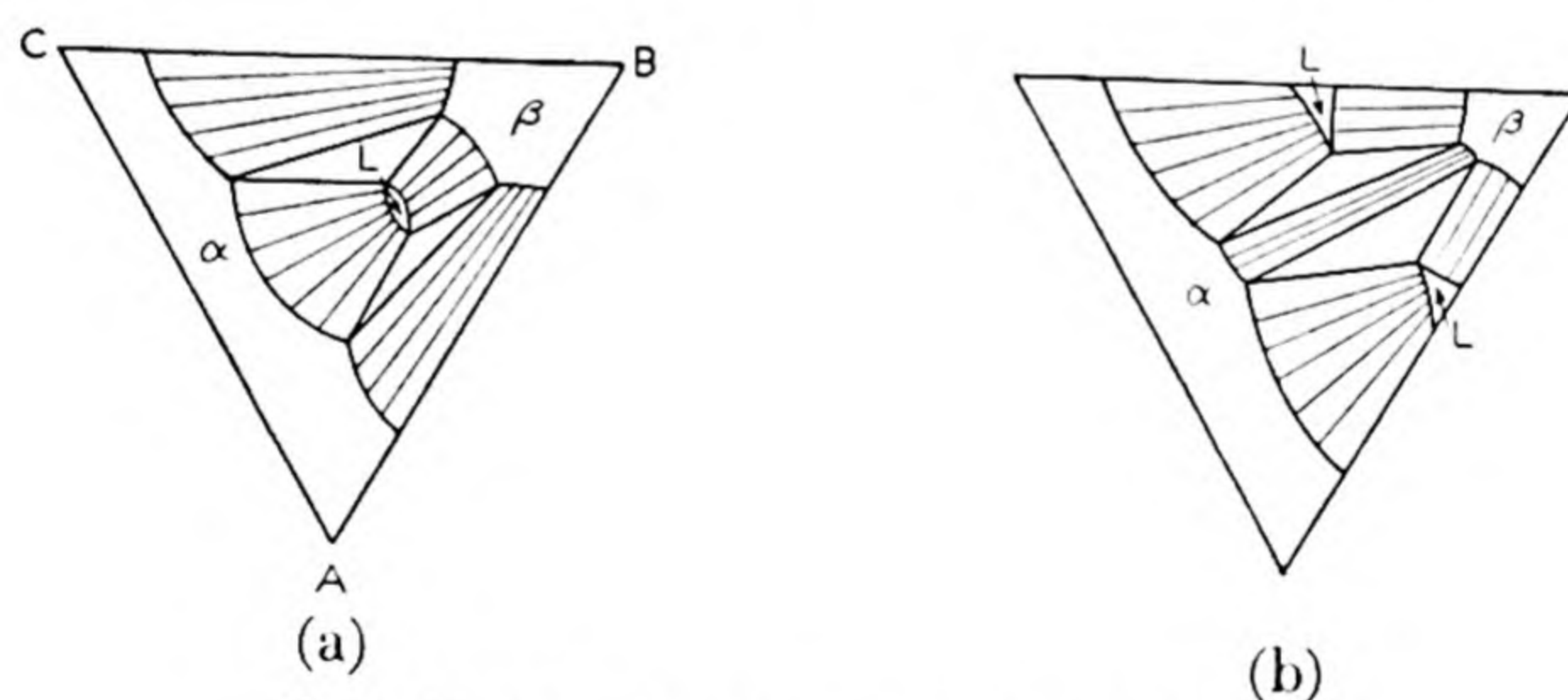


FIG. 11-11. Isotherms of Fig. 11-10.

vapor pressure at constant T , and correspondingly the 2-liquid system of either minimum or maximum boiling point at constant P .

A vertical section of the ternary prism corresponding to the line xmy is shown schematically in Fig. 11-10(c) for the $(P/c)_T$ and in Fig. 11-10(d) for the $(T/c)_P$ relations; these two diagrams are labeled for the liquid-vapor transition. Although xmy is either the minimum or the maximum boiling point of the 2-liquid equilibrium it is still in either case the minimum boiling

point of the section of Fig. 11-10(d), which is simply the ternary case for the "Type IV" relations of 2-liquid systems, discussed under Fig. 4-8(b). For sections on either side of the line xmy the central relations remain as in Fig. 11-7(a).

If xmy is the minimum boiling point of the 2-liquid equilibrium it is also, in the present system, the absolute minimum of the liquid-vapor relations of the ternary system. If it is the maximum-boiling 2-liquid system then it is neither a minimum nor a maximum of the ternary system, which in the present case would have as its minima the two binary equilibria aeb and $a'e'b'$. (For an example in which xmy represents a maximum-boiling 2-liquid equilibrium we may cite the system water (A)-meta-xylene(B)-formic acid (C), with an azeotropic maximum-boiling solution in the continuous binary system A-C; with all arrows reversed except for AC and ee' and with transition paths shaped as in Fig. 11-17(b), Fig. 11-10(a) gives the distillation paths, with m a saddle point on the vaporous surface.¹)

If a 2-liquid system with composition in the region $aa'b'b$ of Fig. 11-10(b) is boiled and if the vapor, with composition always on the curve ee' , is removed as it is formed during the process, the liquids proceed away from the points x and y if xmy is a minimum-boiling equilibrium, and toward one of the binary sides; during the process one of the two liquids may be consumed before the other to leave the system $L+V$. The boiling liquids proceed toward xmy if this is an equilibrium of maximum boiling point, but again one of the liquids may be consumed before the maximum is reached. In either case, the residual liquid will be α , on the curve aa' , if the original total composition is on the AC side of the curve ee' ; for original compositions the B side of ee' the residual liquid is β on the curve bb' . When the residue becomes a single liquid, the compositions of liquid and vapor leave the curves just mentioned, and the boiling point of the system rises toward one of the absolute maxima of the ternary system, in the present case pure B for systems originating on the B side of ee' or the binary AC azeotrope m_1 for systems originating on the AC side of ee' .

The colinear $L_\alpha VL_\beta$ equilibrium here explained, which is always a "constant-boiling" mixture of the ternary system, is sometimes called a "heteroazeotrope" or even simply a "ternary azeotrope." This is rather unfortunate, for a ternary azeotrope, as defined in Chapter X, is a ternary liquid in equilibrium with a vapor of the same composition, and an absolute maximum or minimum of the liquid-vapor transition surfaces. In the present case the vapor m differs from both liquids, x and y , in composition; furthermore the composition of the liquid mixture is variable, although the com-

¹ W. Reinders and C. H. de Minjer, *Rec. trav. chim. Pays-Bas*, **66**, 572 (1947).

position of each individual phase is fixed, during the constant-boiling process.

In the system alcohol–benzene–water the 3-phase equilibrium $L_\alpha VL_\beta$ originating at the binary side of the system benzene–water proceeds into the $(T/c)_P$ prism with decreasing boiling point at atmospheric P . The system differs from Fig. 11-10 merely in that the MG involves only one binary system and closes before reaching another binary side of the prism. (The full relations of such a system will be considered in the last section of this Chapter.) Before the MG closes, however, the normal boiling point of the 2-liquid system passes through a minimum, at a colinear equilibrium of the type of Fig. 11-10. It is this colinear 3-phase equilibrium of minimum boiling point that is commonly referred to as the “ternary azeotrope” of the system alcohol–benzene–water. Yet it is entirely possible for such a system to have a true ternary azeotrope in the homogeneous liquid field outside the binodal region. We find a 2-liquid binary system, which necessarily boils at constant T , similarly called an “azeotrope” (or “hetero-azeotrope”), and yet, as seen in Figs. 4-5(b and c) such systems may have in addition a true azeotrope (point m).

2. The MG Is Peritectic at Both Ends (Figs. 11-12, 11-13, 11-14)

Fig. 11-15 shows four schematic isotherms, with C assumed $> p$. The curve pp' of Fig. 11-13 divides the β liquidus from the α liquidus; the solidus

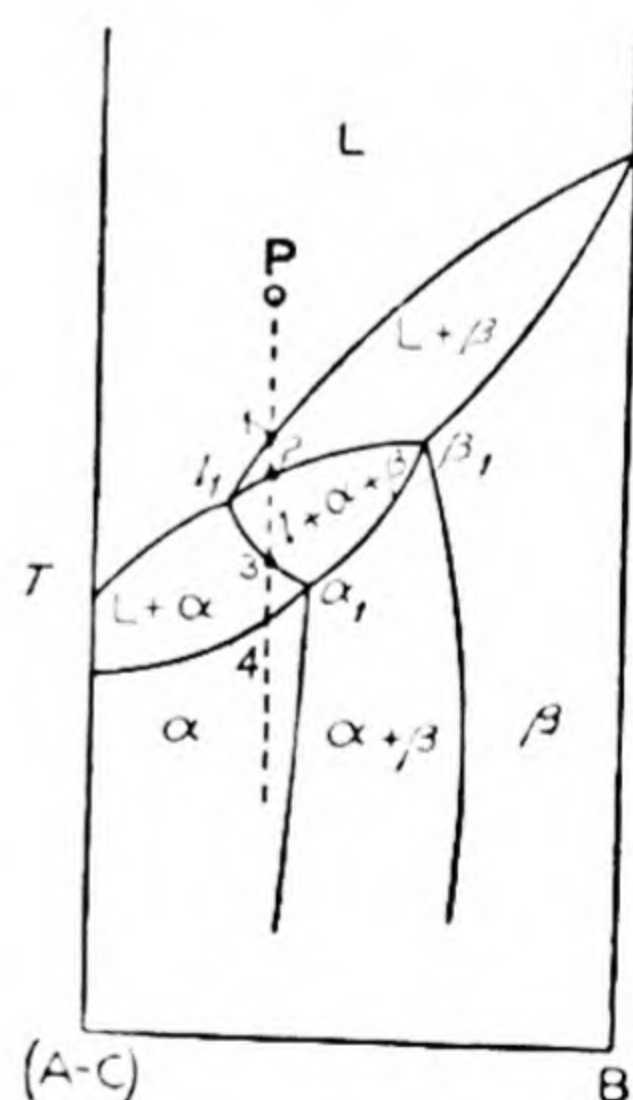
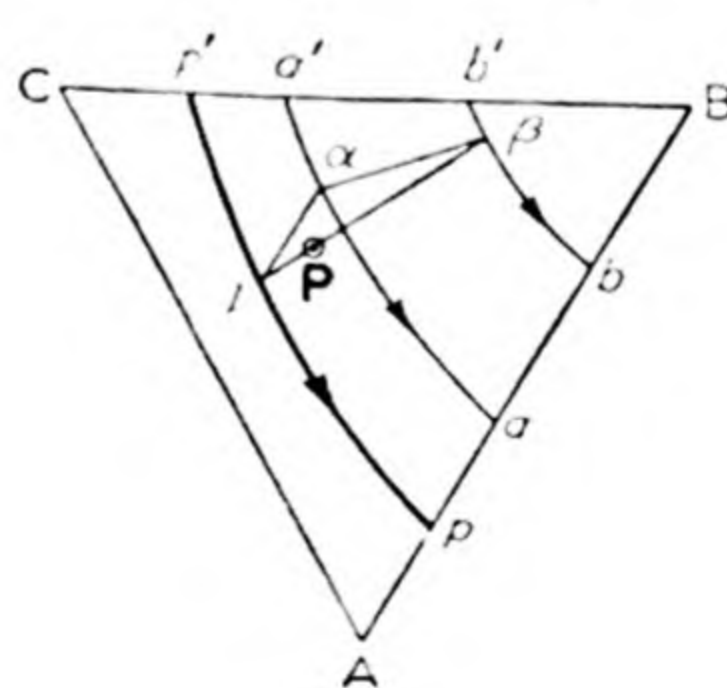
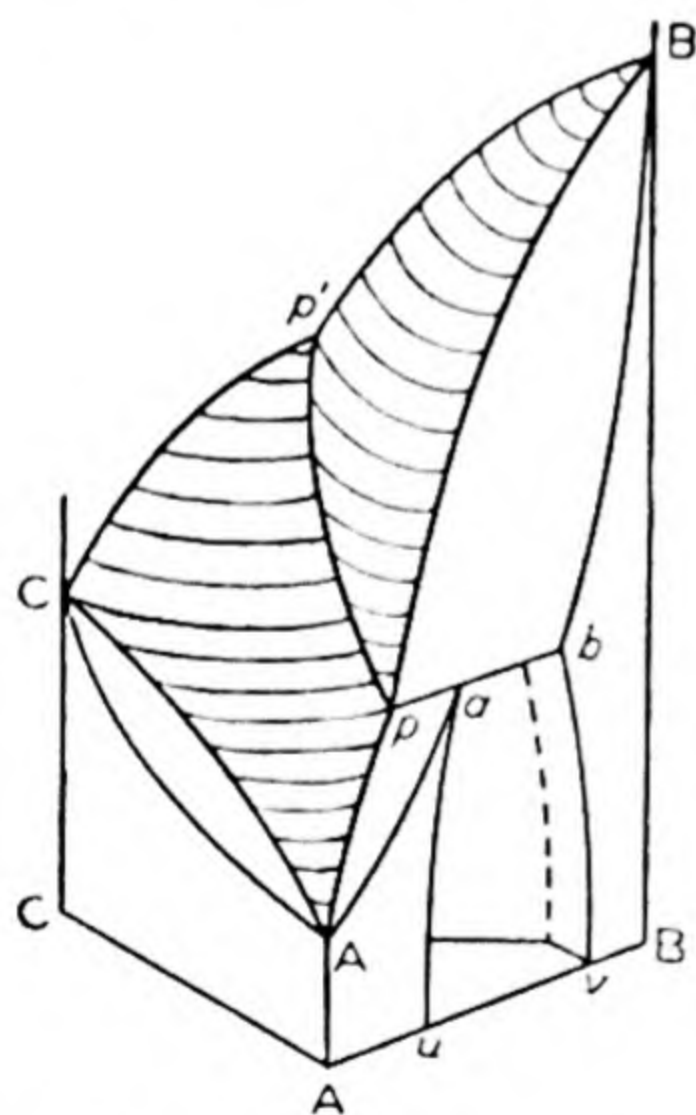


FIG. 11-12. MG between two binary systems (both peritectic).

FIG. 11-13. Polythermal projection of Fig. 11-12.

FIG. 11-14. Vertical section of Fig. 11-12.

surfaces remain as in Fig. 11-6, Bbb' for β and $Aaa'C$ for α . If the original composition P of a liquid falls in the projection of a solidus surface it must, with complete equilibrium, ultimately solidify to a single solid; two solids, or a mixture of α and β , will result only if P falls in the MG , $abb'a'$ of Fig.

11-13. The primary crystallization product is determined by the liquidus surface in which **P** falls; the ultimate solids depend on whether **P** is in the *MG* or in one of the solidus surfaces.

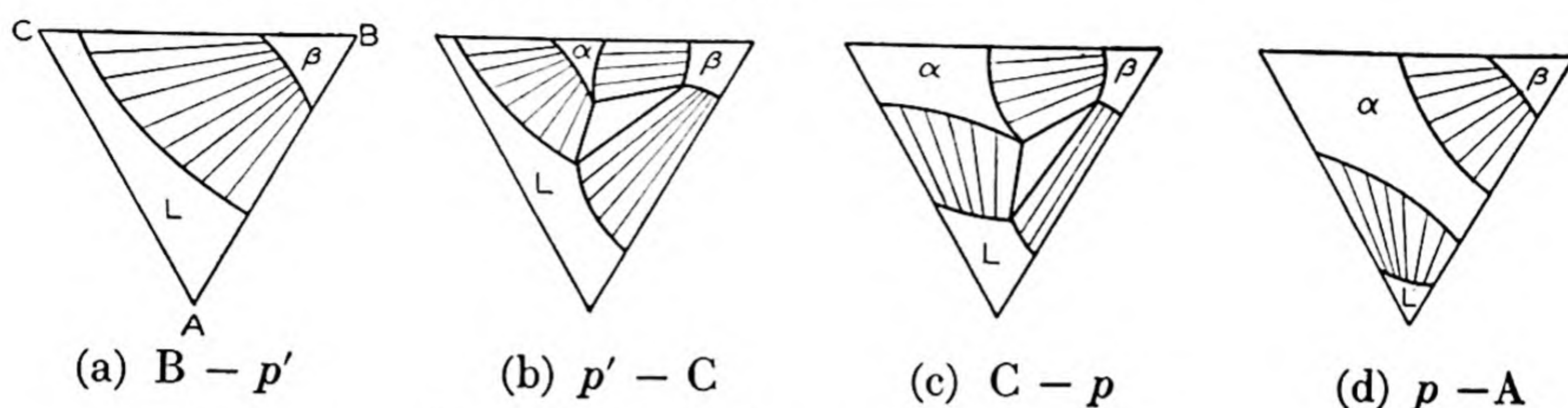


FIG. 11-15. Isotherms of Fig. 11-12.

In the present case, therefore, if **P** is in the β solidus, the only process, for equilibrium, is precipitation of β , and the liquid, although changing in the direction of the curve pp' , is consumed before reaching this curve. The curve pp' is reached only by liquids in the region $pbb'p'$, while precipitating β . Such liquids reach the curve and begin to precipitate α , just as the accompanying solid solution reaches the curve bb' . Then the reaction $l + \beta \rightarrow \alpha + \text{cals.}$ proceeds, the three phases moving in composition along the curves of Fig. 11-13 until either l or β is consumed: l for those in the *MG*, leaving $\alpha + \beta$, and β for those, such as **P** in Fig. 11-13, in $pp'a'a$, leaving $l + \alpha$ when **P** is swept by the line $l\alpha$. In the latter case the liquid then crosses the curve to enter upon the α liquidus and is consumed when

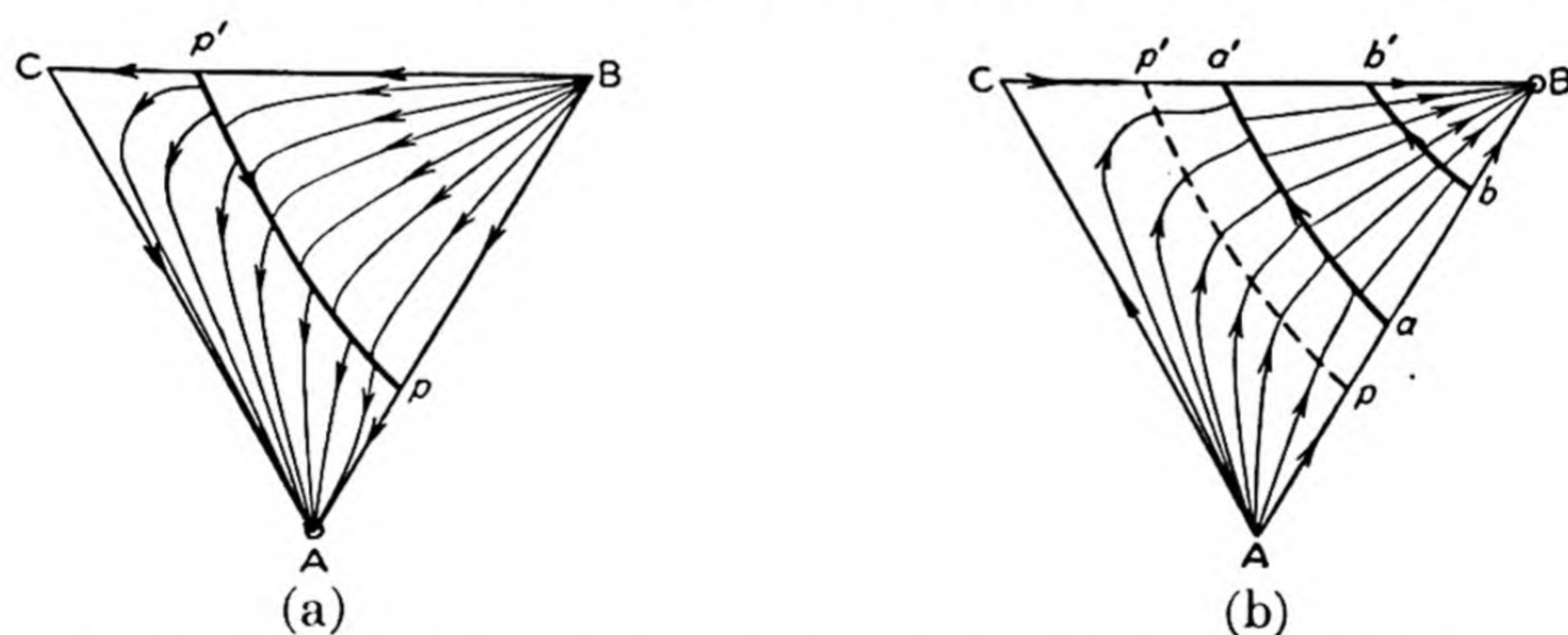


FIG. 11-16. Transition paths for the system of Fig. 11-12.

the solid phase, now α , attains the composition **P**, on the α solidus. The temperatures of the four successive breaks in the cooling curve of the point **P** of Fig. 13 may be seen in Fig. 11-14, a vertical section through **P**; there are only three thermal breaks if **P** falls in the *MG*. Finally, liquids in the area $App'C$ of Fig. 11-13 precipitate α as sole solid phase, and solidify completely while traveling in the general direction of point A.

For crystallization and boiling point paths, we have Fig. 11-16(a) and

(b), respectively. In distillation (11-16(b)), liquids with compositions in the field $Aaa'C$ (α liquid) change in composition until the curve aa' is reached, when the β liquid appears. Now the two conjugate liquids change along the curves aa' and bb' , while giving off a vapor on the curve pp' , until the original α layer is consumed, and then the residual β liquid leaves the curve bb' while the boiling point rises still further toward B.

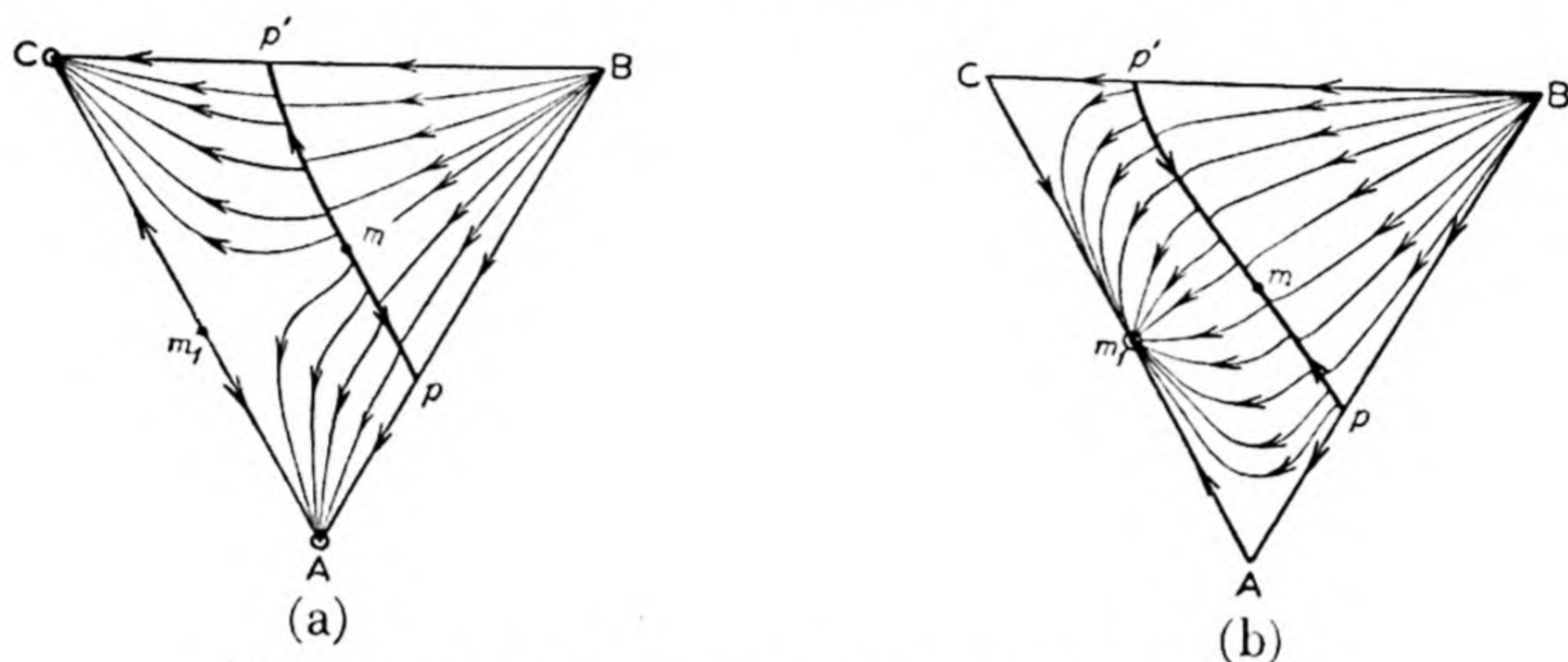


FIG. 11-17. Azeotropic variations of Fig. 11-16.

The peritectic curve, or the 3-phase system $l\alpha\beta$, may have either a maximum or a minimum accompanying usually an azeotropic relation in the binary system A-C. The maximum will be above the maximum of the A-C system, and the ternary minimum will likewise be above the binary minimum. Fig. 11-16(a) becomes 11-17(a) for the maximum, and Fig. 11-17(b) for the minimum, case. Fig. 11-18 shows schematic isotherms:

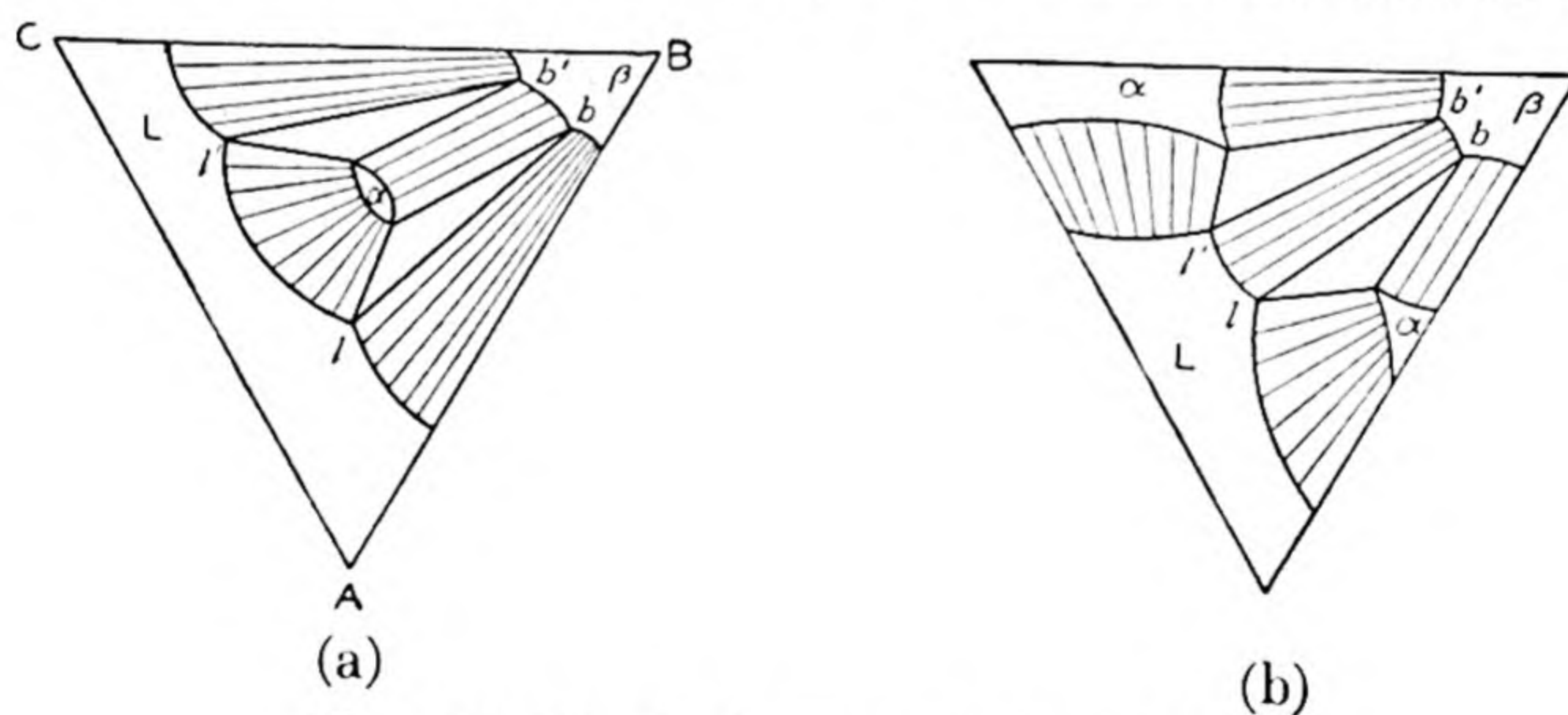
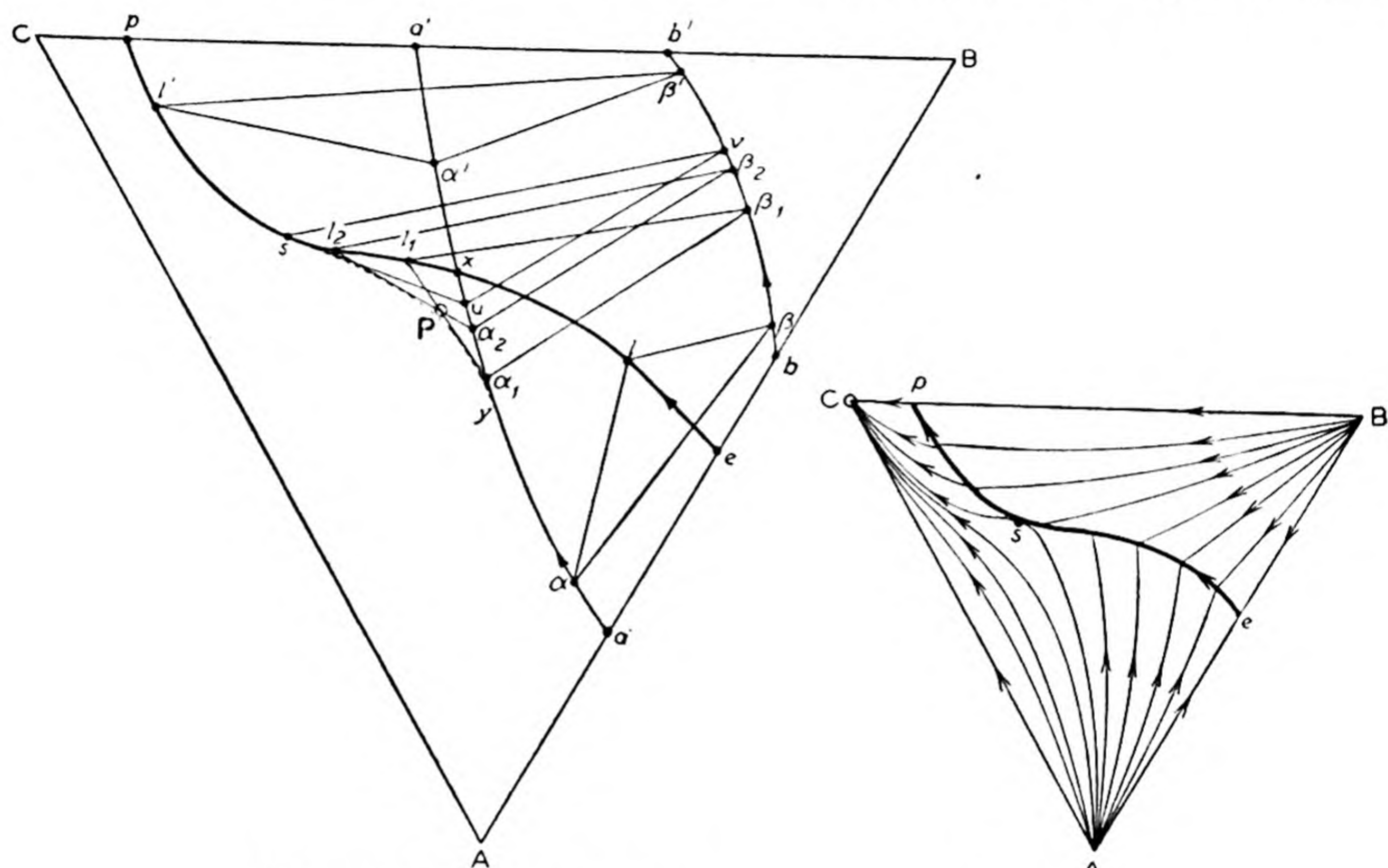


FIG. 11-18. Isotherms of Fig. 11-17.

(a) just below a maximum, and (b) just above a minimum. As the temperature of Fig. 11-18(a) is raised, the two 3-phase triangles vanish to lines at the same time that l merges with l' and b with b' ; at this temperature maximum of the pp' curve the α field of Fig. 11-18(a) vanishes in a colinear equilibrium, leaving 11-15(a). As the temperature of Fig. 11-18(b) is lowered, the two 3-phase triangles similarly vanish to lines as l merges with l'

crystallization product, but with continued cooling the liquid and solid change in composition until at some temperature T_1 the liquid lies at l_1 on the section sx of the curve ep and the solid at α_1 on the section uy of the curve aa' , when therefore a second solid, the β phase, begins to form,



(a) polythermal projection

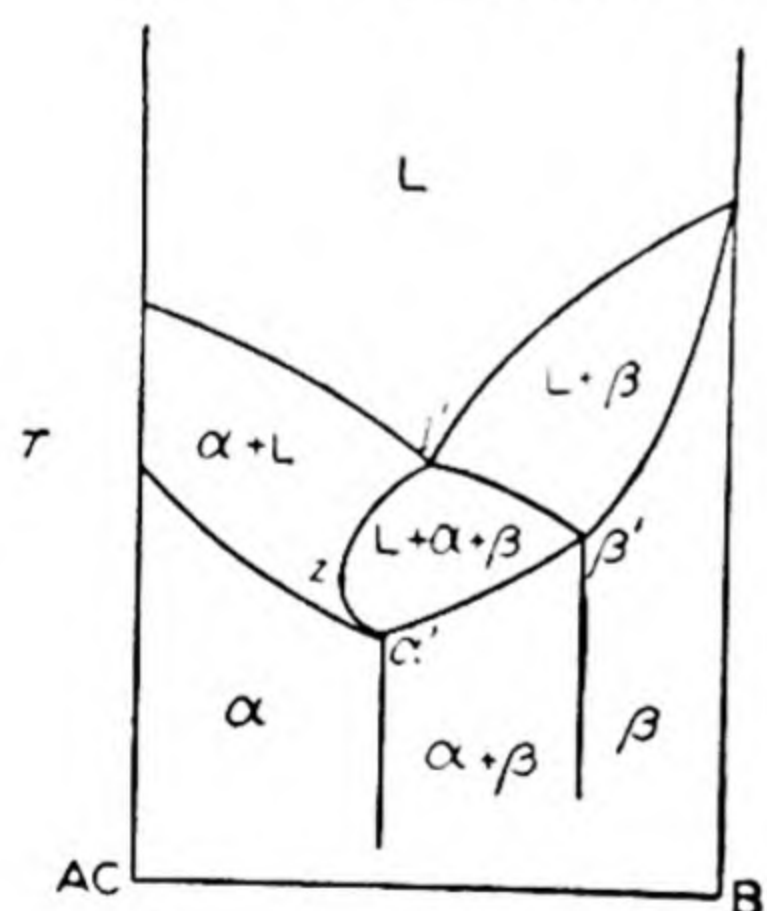
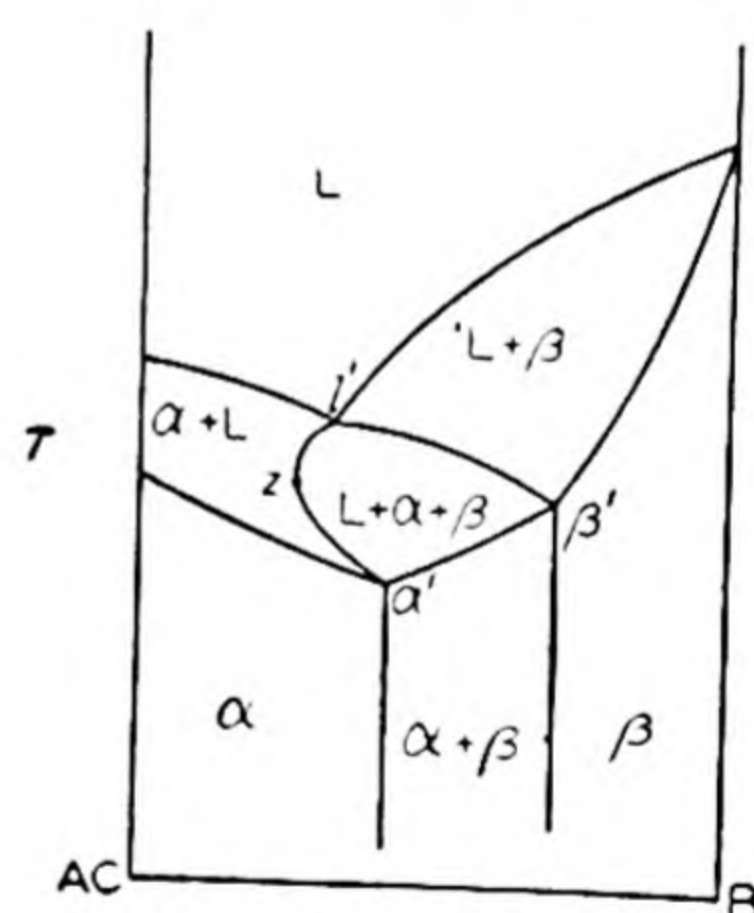
 (b) $Ph\ 2$ surface

 (c) vertical section between y and x

 (d) vertical section between x and s

FIG. 11-20. Temperature falling from eutectic to peritectic.

with composition β_1 on bb' . While the liquid is in twofold saturation, its composition moves toward p and the solids move toward a' and b' , as cooling is continued. For a certain temperature range, $T_1 - T_2$, the system therefore exists in three phases. But since this envelope region is outside the MG the point P comes again to be swept by the $l\alpha$ tie-line, so that at T_2 the β phase disappears again, with composition β_2 , and the liquid l_2 , now

saturated only with α_2 , leaves the curve. It reenters upon the α liquidus and it is there consumed to leave α solid. If P is in the region suy , the curve is left along its even section, xs , while if P is in sxu the curve is left along its odd section sp , so that such compositions behave just as do those in the area $spa'x$.

We may note, therefore, that although an even curve of twofold saturation is never left during crystallization with effective removal of solid even if the solids are variable in composition, it may be left by the liquid if the process, involving variable solids, is one of complete equilibrium. In equilibrium transition involving variable phases, a twofold saturation curve, whether odd or even in reaction, may, moreover, be left on either side. This is in accord with the distinction made in Chapter X, section B: that while the crystallization path for effective removal of solid is unique for a liquid of given composition, such as a point on a twofold saturation curve, there is no unique path for this same liquid in a process of equilibrium solidification involving variable solid phases. The path depends on the total composition. Hence a liquid on such a curve will continue on the curve, thereby following a unique path, only as long as both solids are present; but if one solid is consumed the liquid may leave the curve, whatever its type, for either side, depending on the solid phase left, and therefore on the total composition of the complex.

The appearance of the vertical section from B to the AC side changes from that in Fig. 11-7(a) to that in Fig. 11-14, as we travel from e to p with falling T . The liquidus for saturation with the α phase first falls toward the twofold saturation curve ep and later, beyond s , rises toward it. A section passing between y and x appears as in Fig. 11-20(c) and one between x and s as in Fig. 11-20(d). The curve $l'\alpha'$, which also appears in Fig. 11-7(a) and Fig. 11-14, is seen to bulge out to the left in these sections. It represents a series of points on the $l\alpha$ tie-lines between y and s , and the extreme point z is in each case projected as on the envelope sy in Fig. 11-20(a). It is here seen that the equilibrium cooling of a liquid with composition between z and α' in Fig. 11-20(c) and between z and l' in Fig. 11-20(d) — and therefore in the region sxy of Fig. 11-20(a) — leads to the following sequence of equilibrium states: $L + \alpha$, $L + \alpha + \beta$, $L + \alpha$, α . In terms of solid phases alone, the sequence is α , $\alpha + \beta$, α .

Finally, we may repeat at this point that the MG , starting from one binary side, may close before reaching another side of the triangle. In such systems, which will be discussed later, the twofold saturation curve may not only pass through a maximum or a minimum of T , but may also undergo change of sign of reaction, with relations similar to those here described.

C. Three Solid Solutions

Each binary system is assumed to have a *MG* at the melting point curve, so that there are three separate fields of solid solution, α , β , γ , according to the corner of the composition plane included in each. With three solids and a liquid, isobarically invariant 4-phase equilibria became possible, which are “quintuple points” of the ternary system with vapor present, if, for example, the diagram is that of the system in open air. These Q-points may arise at the intersection of the 3-solid ($\alpha\beta\gamma$) system, always rising from low T , with three of the equilibria already discussed, of liquid saturated with two solids. As explained in Chapter X, there are two types (*A* and *B*) of such 4-phase invariants (isobaric). The significant phase in freezing equilibria is the liquid phase. If this disappears, as T falls, in a Q-point of type *A* — that is, if the liquid is the interior phase 4 of Fig. 10-23 — the invariant system is called a **ternary eutectic**. Otherwise we shall call it a **ternary peritectic**, specifying the type (*A* or *B*) in addition. The liquid cannot disappear at the expense of solids, with increasing T , at such points; but one of the solids may do so, and then the point, type *A*, is terminal in respect to that particular solid.

A peritectic, then, may be either a terminal or a diagonal invariant, but it is not terminal in respect to the liquid. The three liquid curves of twofold saturation meeting at a peritectic need not all be “odd” in their crystallization, so long as one falls away from it in T . A eutectic is always type *A*, terminal for the liquid, which is the interior phase of the 4-phase invariant eutectic plane, the “eutectic triangle” of the three solids, which we shall call a , b , c . The three liquid curves meeting (and ending) at the eutectic will all be even in reaction, generally positive for both solid phases. This follows from certain principles stated in connection with Figs. 11-26 and 11-27, and it will be obvious if the solids are the pure components.

Furthermore, the eutectic liquid, with composition falling inside the triangle of its three solids, is said to be “congruently saturated” with its three solids; it constitutes then a “congruent” solidification or crystallization end-point on cooling, for compositions falling inside the “eutectic triangle,” and the invariant eutectic reaction is always $L \rightleftharpoons a + b + c + \text{cals.}$ The composition of the peritectic liquid, however, falls outside the triangle of its three saturating solids, whether the invariant plane is triangular (type *A*) or quadrangular (type *B*), and it is therefore said to be “incongruently saturated” with its three solids. It may be the incongruent solidification or crystallization end-point for certain compositions of the ternary system, namely those falling within the triangle of the three peritectic solids a , b , c , in invariant peritectic reactions such as $L + a \rightleftharpoons b + c + \text{cals.}$

for the more common type *B* or quadrangular case, and such as $L + a + b \rightleftharpoons c + \text{cals.}$ for the type *A*, triangular case.

1. All Three Binary Systems Eutectic

As the three eutectic curves of twofold saturation enter the T/c prism, they divide the freezing point or solubility surface (that is, the liquidus) into three parts, one for each of the three solid phases. If they all fall in T , the three curves meet at the minimum point, the eutectic solution E , the interior phase of the isothermal, 4-phase eutectic triangle. Each liquid curve leading to this point is the leading corner (l) of a 3-phase triangle of the type of Fig. 11-1(a). Every corner then of the eutectic triangle is the intersection of three solid-composition curves: at the α corner, for example, the α phase of the triangle $l\alpha\beta$, the α phase of the triangle $l\alpha\gamma$ (these reaching the eutectic from higher T), and the α phase of the triangle $\alpha\beta\gamma$, coming from lower T .

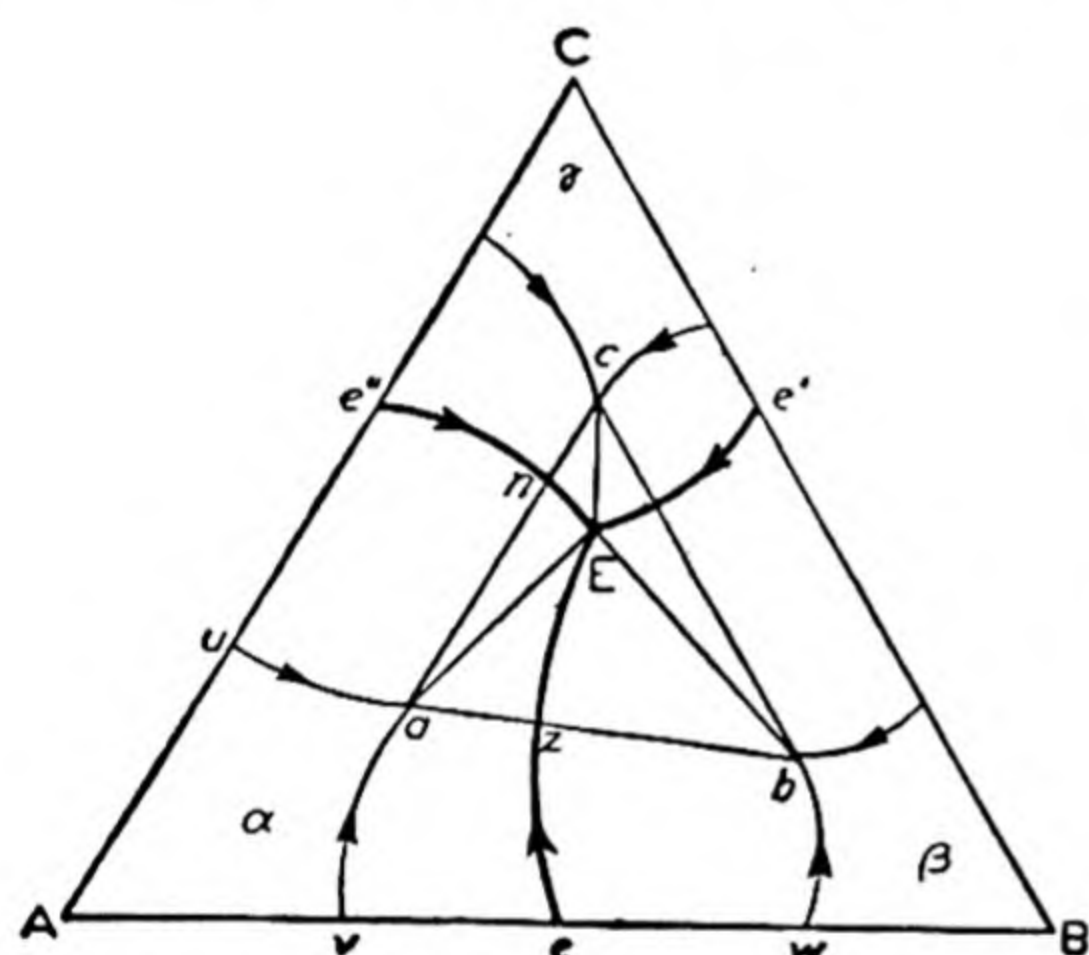


FIG. 11-21. Three solid solutions with ternary eutectic.

The 3-phase equilibria originating at the binary eutectics are shown in projection in Fig. 11-21. Each of the final 3-phase triangles abE , acE , bcE , originated at a binary side as a binary eutectic tie-line and proceeded, with falling T , into the prism, all three meeting to form the 4-phase, isothermal invariant plane abc with the liquid E inside, at the eutectic temperature. The course of the corners of the triangle of the 3-phase system $\alpha\beta\gamma$, rising from low T , is

not shown, but these corners coincide with the points a , b , c of Fig. 11-21, at the eutectic T . If all the temperatures of the binary eutectics are lower than the melting points of the pure components, and if their order is $e > e' > e''$, the typical isotherms are those of Fig. 11-22.

If a liquid with composition in the field $Ae''Ee$ is cooled, it produces α solid in primary crystallization when the temperature reaches that of the α liquidus surface for the specified composition. Through the appropriate isotherm of the system, the tie-lines of the $\alpha + L$ region involved may be used to find the composition of the initial trace of α solid formed. As T falls, liquid and solid both change in composition. If the total composition lies in the section $Auav$, the liquid solidifies completely before a curve of twofold saturation is reached, and leaves an α solid solution as sole solid phase; the cooling curve has the schematic form of Fig. 11-23(a). If the composition lies in the section $avez$, it must end up as a mixture of α and β phases and

will therefore reach, carrying α solid as primary crystallization product, curve eE to precipitate β as the second solid phase. During simultaneous

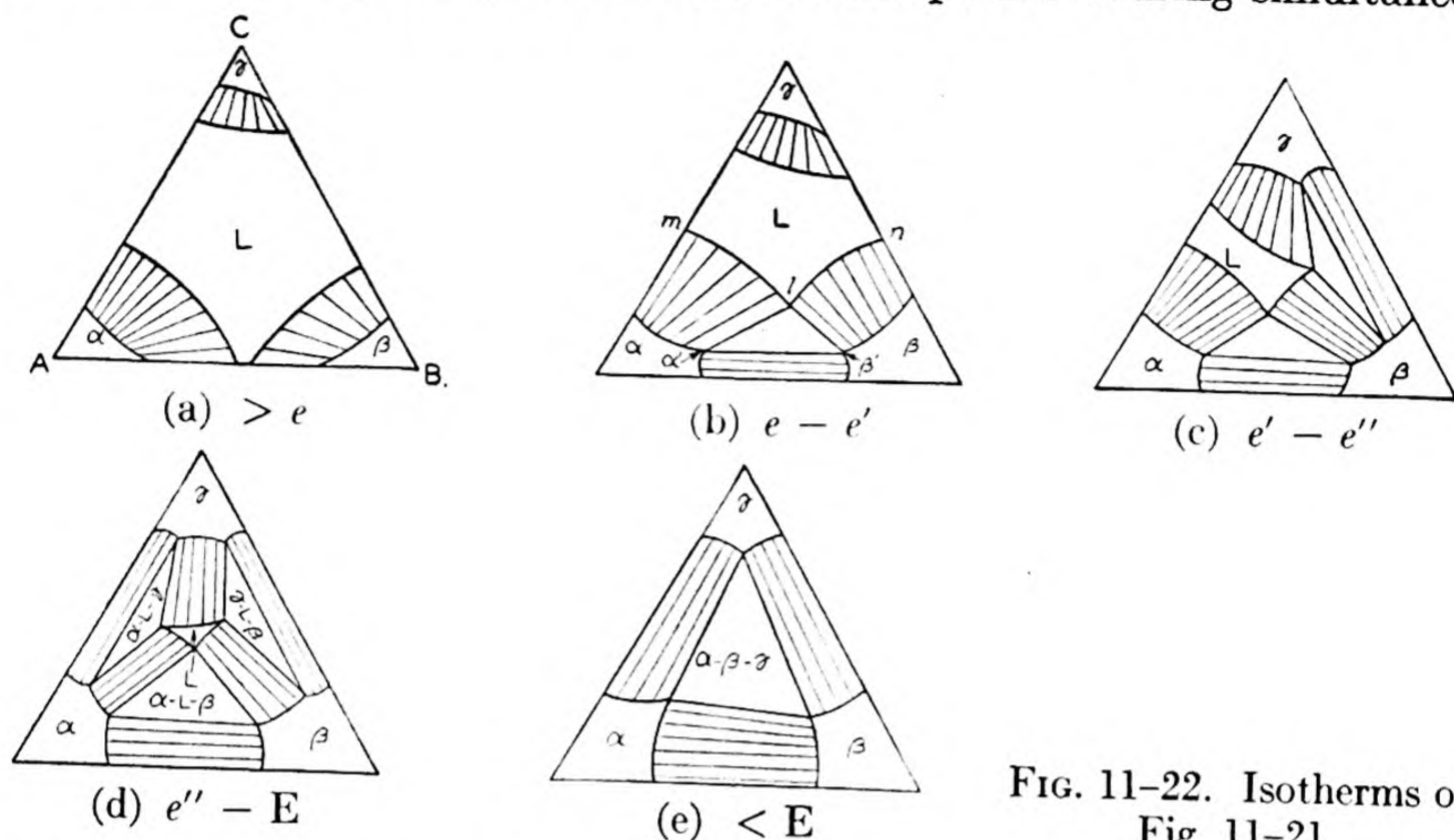


FIG. 11-22. Isotherms of Fig. 11-21.

precipitation of α and β , with compositions on the curves va and wb respectively, the liquid moves on the curve eE toward E . But the liquid is consumed before E is reached, leaving the mixture $\alpha + \beta$, on a tie-line passing through the composition of the original liquid, which therefore also fixes the temperature of final solidification; the cooling curve is shown in Fig. 11-23(b). Finally, if the original liquid has a composition in the section

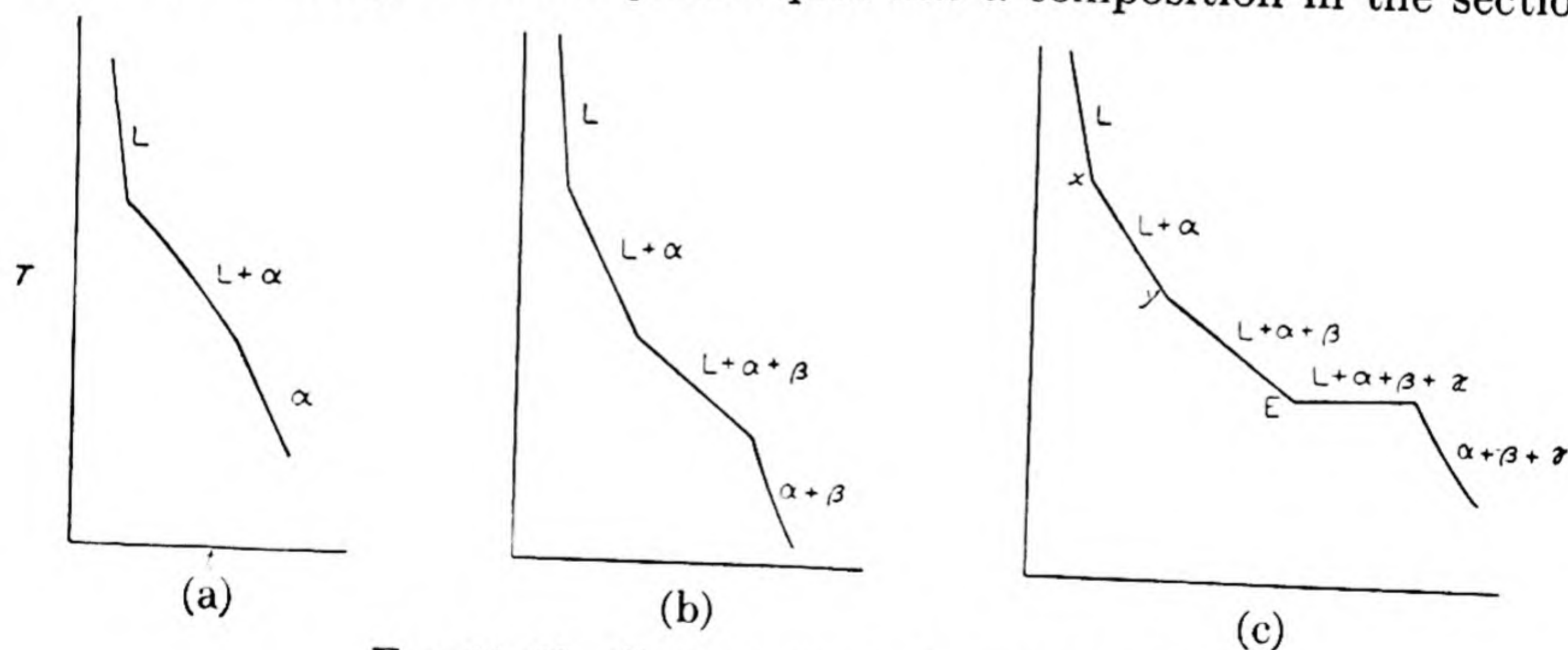


FIG. 11-23. Cooling curves for Fig. 11-21.

$azEn$, it will give either β or γ as second solid phase, and this depends on the total composition and on the courses of all the tie-lines involved as T changes. But in either case the liquid reaches E , at the same time that the two solid phases accompanying it reach their respective corners of the eutectic triangle. Then a third solid (c or b) begins to precipitate together

with more of the first two, and the liquid reaching E solidifies (isobarically) at constant temperature and with constant composition (Fig. 11-23(c)). The duration of this eutectic halt in thermal analysis depends, for a given system, on the quantity of liquid reaching E and hence, in general, on the closeness of the original composition to the point E. From the total composition the relative amounts of the three phases a , b , c , finally obtained, may be calculated.

Finally, if the solid is not given time to adjust its composition during the solidification process, but may be considered out of the equilibrium, then a liquid with composition falling anywhere in the α field, $Ae''Ee$, precipitates α solid and may reach one of the "eutectic curves," $e''E$ or eE , and finally the eutectic E itself. This is shown in Fig. 11-24(a), giving the crystallization paths of the liquidus surface.

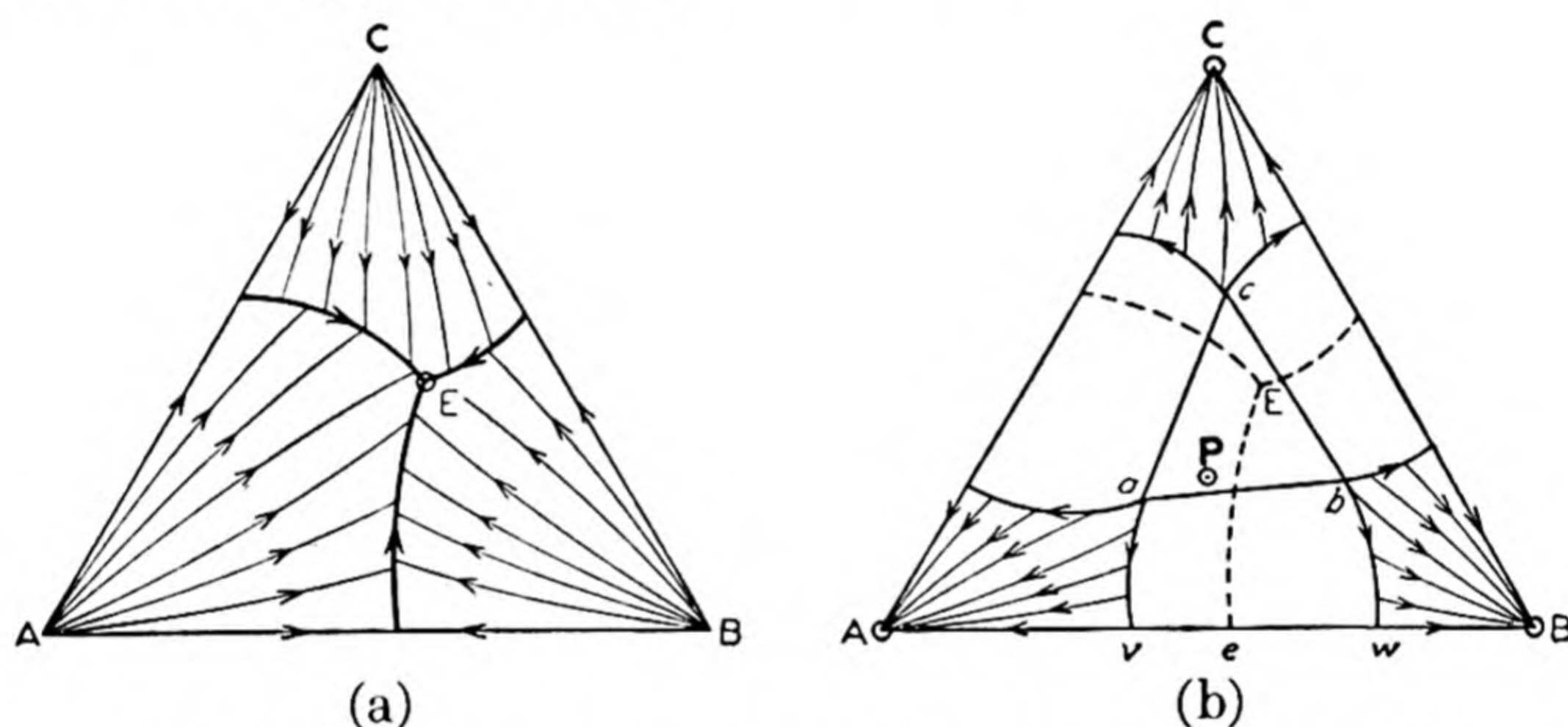


FIG. 11-24. Transition surfaces of system of Fig. 11-21.

Fig. 11-24(b) shows the reverse process (rising T) applicable to the distillation of three partially miscible liquids. Mixtures of three liquid phases, falling in the triangle abc , boil at the same, constant T . If the composition of the original mixture is P , then, as the vapor with composition E is removed, the composition of the residual 3-liquid mixture moves away from E on the line EP until the line ab is reached, when the liquid c will have been consumed. Now the boiling point begins to rise, while the liquids change in composition along the curves av and bw . But as vapor (on curve Ee) is removed, the β liquid is consumed, leaving a single liquid (α) on the curve av . As the distillation proceeds further, the residual liquid approaches pure A .

A variation of Fig. 11-21 with a temperature maximum on one of the curves of twofold saturation is shown in Fig. 11-25(a) as a polythermal projection; Fig. 11-25(b), to be compared with Fig. 22(c), is the schematic isotherm just above a maximum.^{1a}

^{1a} Discussed by R. v. Sahmen, *Z. phys. Chem.*, **79**, 421 (1912).

A liquid of twofold saturation appears, on an isothermal section, as the intersection of two solubility curves. In Fig. 11-22(b) the curve ml is the solubility curve, at the T of the isotherm, of the α solid, and nl the solubility curve of the β solid; l , their intersection, is a point on the curve eE of Fig. 11-21 and is called an isothermally invariant solution (the pressure always

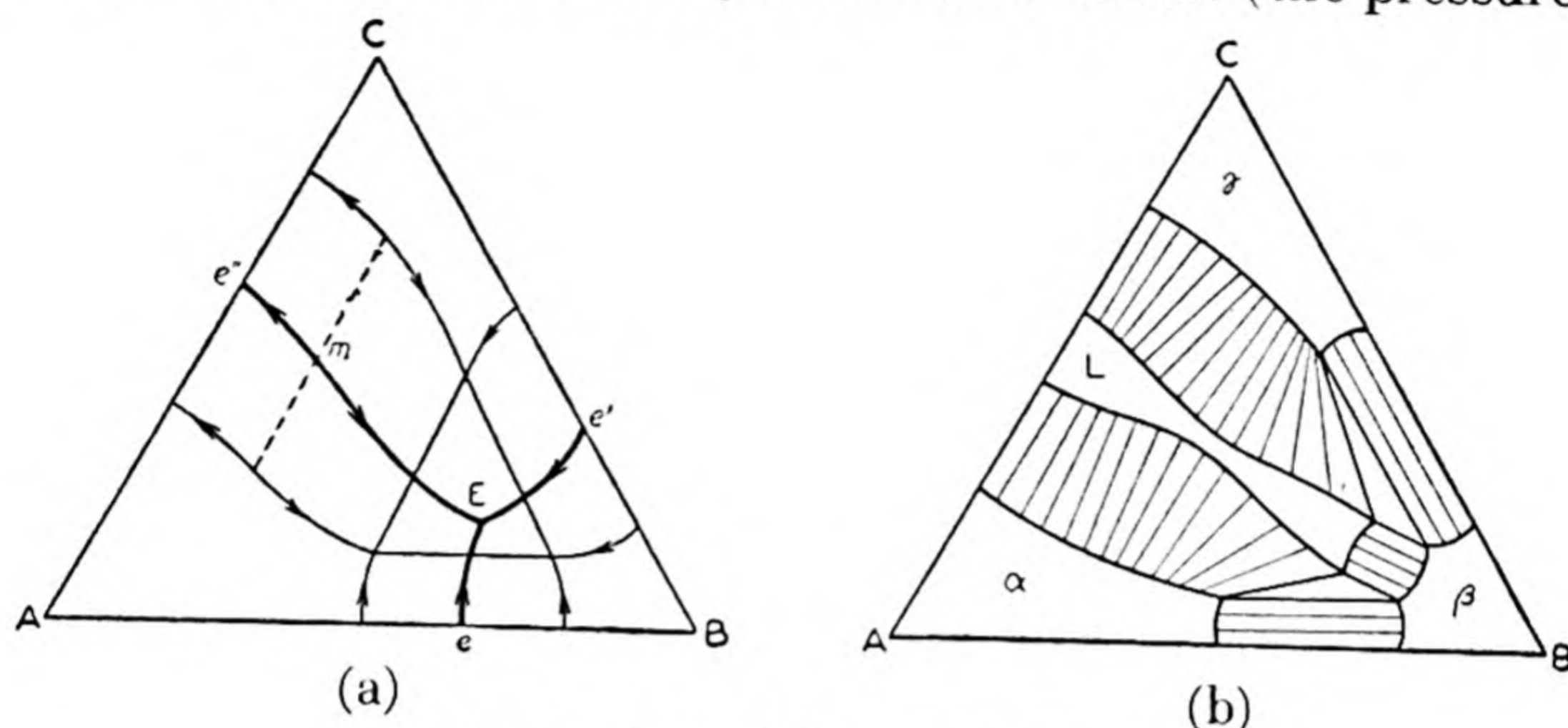


FIG. 11-25. A special case of Fig. 11-21.

being considered constant). All compositions in the triangle $\alpha'l\beta'$ at this temperature give, at equilibrium, the liquid l and a mixture of solid phases of the compositions α' and β' . The angle of the intersection of the two solubility curves, at point l , is always less than 180° , in respect to the field of homogeneous liquid, L . This must be so since the metastable extension of the β curve, or ln , for example, must represent a higher concentration of α in the liquid phase, than that on the α curve, lm , for the solution in metastable equilibrium with β will be supersaturated with respect to α .

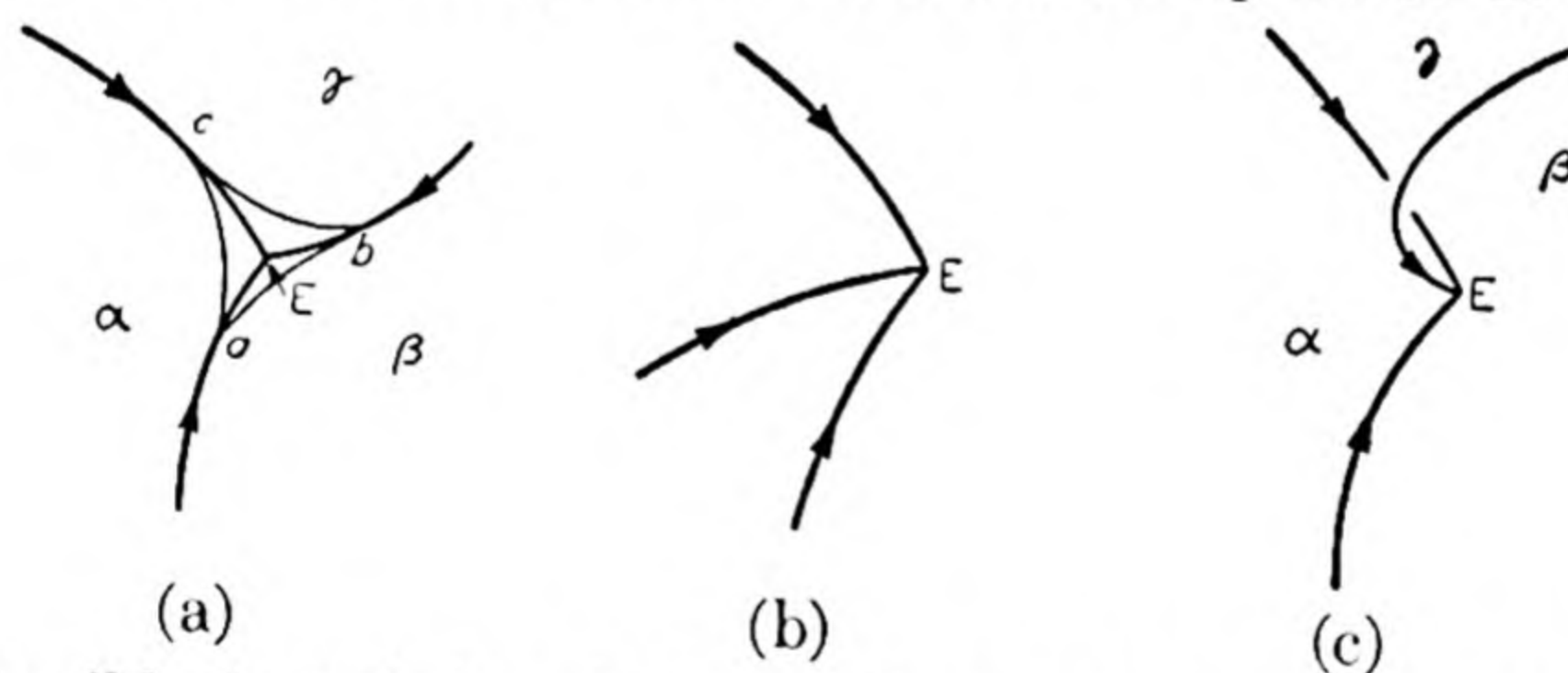


FIG. 11-26. Possible (a and c) and impossible (b) intersections of eutectic curves.

For this reason the configuration of the projections of the three eutectic curves at the eutectic must be as in Fig. 11-26(a), with no angle greater than 180° between two adjacent curves, and not as in Fig. 11-26(b). The curves ab , bc , ca would be the solubility curves, at a temperature just above E , enclosing the isothermal liquid field such as that of Fig. 11-22(d). The apparently exceptional case of Fig. 11-26(c) is possible and arises when the curve for liquid saturated with respect to β and γ passes through a minimum

(measured from the α corner to the $\beta\gamma$ base) as the temperature changes (cf. Fig. 11-3(c)). This case is to be compared with the binary analog, Fig. 5-2(b). But in the absence of such a retrograde solubility effect, case (a) is the only possibility if the liquid E is to be inside the Q -triangle and if the isothermal solubility curves are to intersect with required angles ($< 180^\circ$), at the points of twofold saturation.

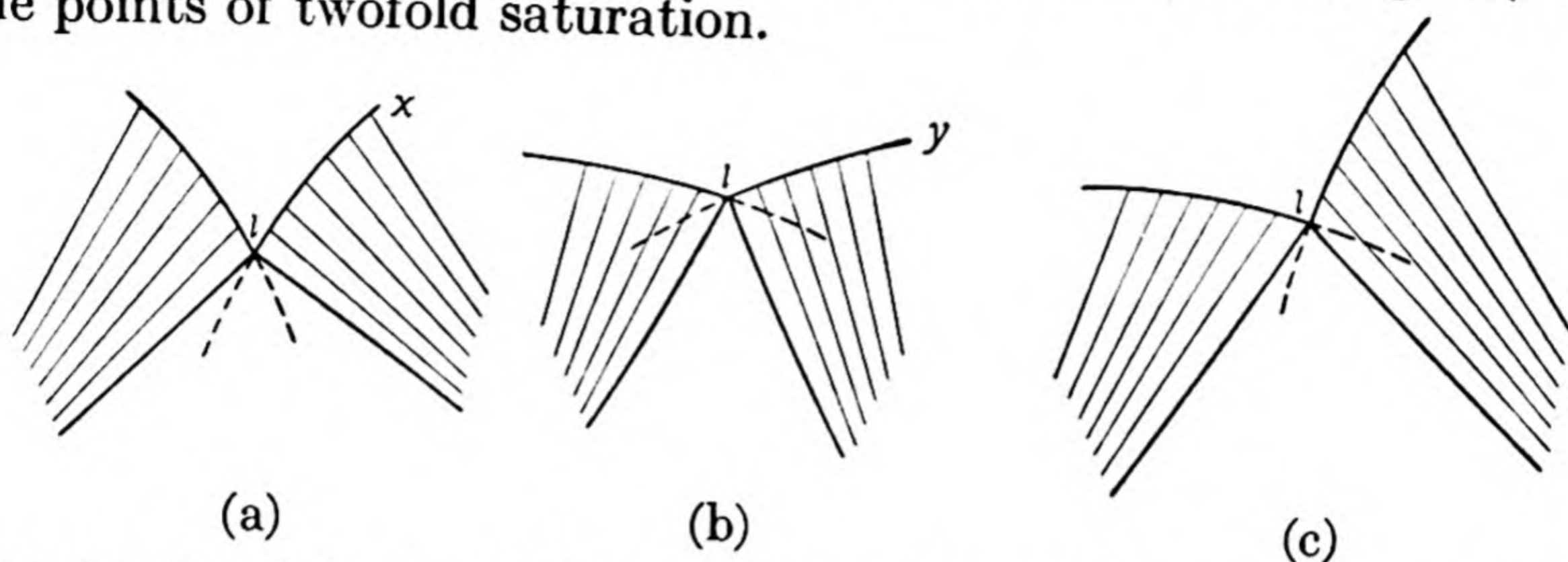


FIG. 11-27. Possible (a and b) and impossible (c) intersections of isothermal solubility curves.

Schreinemakers² has pointed out further limitations on the configuration of the lines ml , nl , $\beta'l$, $\alpha'l$ at the point l , in an isotherm such as Fig. 11-22(b). The arrangements shown in Fig. 11-27(a) and (b) are possible, that in Fig. 11-27(c) impossible. The tangents of the two solubility curves at their intersection, point l , must both lie inside or both outside the isothermally invariant area. This is so regardless of the nature of the saturating phases involved, whether solid or liquid, and whether pure components, solid solutions, or compounds. In (a) it may be seen that α and β , in the immediate vicinity of point l , increase, while in (b) they decrease, each other's solubility. If the α phase, for example, is added to and dissolved in the solution x , which is saturated with β , the total composition is brought into the unsaturated area, and β dissolves. On the other hand, if the α phase is added to the solution y , also saturated with β , the total composition is brought into the heterogeneous field $L + \beta$, and β is caused to precipitate. In (c) they would be exerting opposite effects on one another, and this is thermodynamically impossible, somewhat in the sense that in a binary liquid, for example, the fugacities of the two components must deviate from ideality in the same direction. The isothermal configuration along a curve originating at a binary eutectic, whether rising or falling in T , must start as in Fig. 11-27(a) (cf. Fig. 11-8(c)), while that along a curve originating at a binary peritectic, on the other hand, always starts as in Fig. 11-27(b) (cf. Fig. 11-15(b)).

² F. A. H. Schreinemakers (Ref. P), Vol. III, Part 1, 71-74, 260-270; see also E. D. Williamson and G. W. Morey, *J. Am. Chem. Soc.*, **40**, 49 (1918), for derivation of the theorem.

If all the melting points and eutectics of the systems A-C and B-C are higher than the AB eutectic (Fig. 11-28), it is possible for the even reaction curve from e (system A-B) to rise in T into the prism, and meet the other two at a ternary peritectic point Q_B (diagonal type invariant) (Fig. 11-29). Above Q_B , the 3-phase equilibria are $\alpha\gamma L$ and $\gamma\beta L$, falling to Q_B as even-type triangles; one or both of these may become odd curves before reaching the invariant. Below Q_B , the 3-phase equilibria are $\alpha\beta L$, falling away as an even-reaction curve, and $\alpha\beta\gamma$, the 3-solid equilibrium, starting from Q_B as the triangle abc . Isotherms are shown in Fig. 11-30: (a) above Q_B , and (b) below Q_B . The primary crystallization product on cooling a liquid depends on the composition of the liquid with respect to the crystallization surfaces projected as the fields $Ae''Qe$, $eQe'B$, $Ce''Qe'$, in Fig. 11-29. Furthermore, those falling in the sections labeled α , β , γ of Fig. 11-29(a), such as $Aa'ax$ for α , solidify completely before reaching any curve of twofold saturation. Those in the field $xyca$ reach the curve $e''Q_B$, but solidify com-

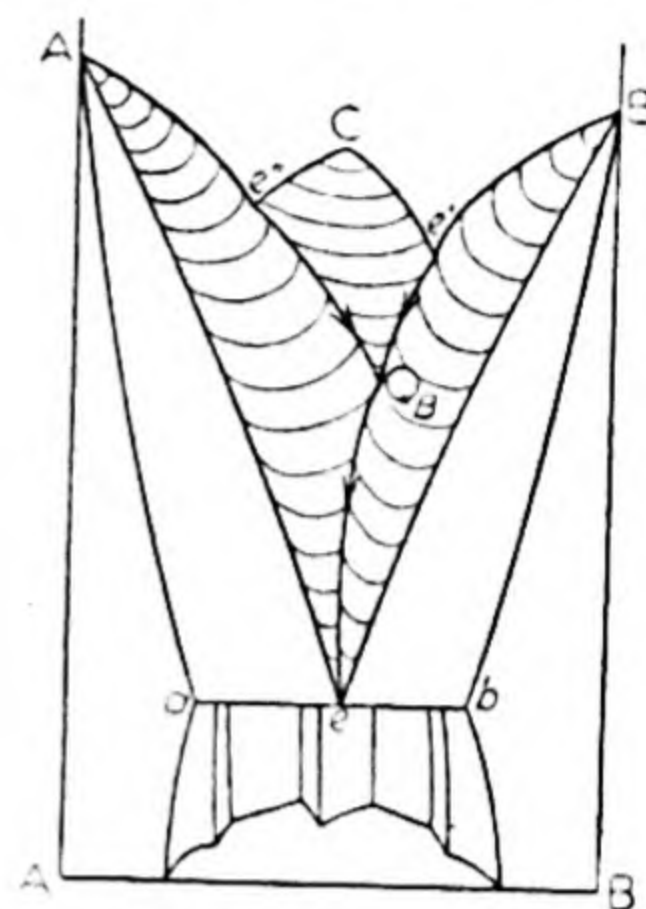


FIG. 11-28. Three binary eutectics with ternary peritectic.

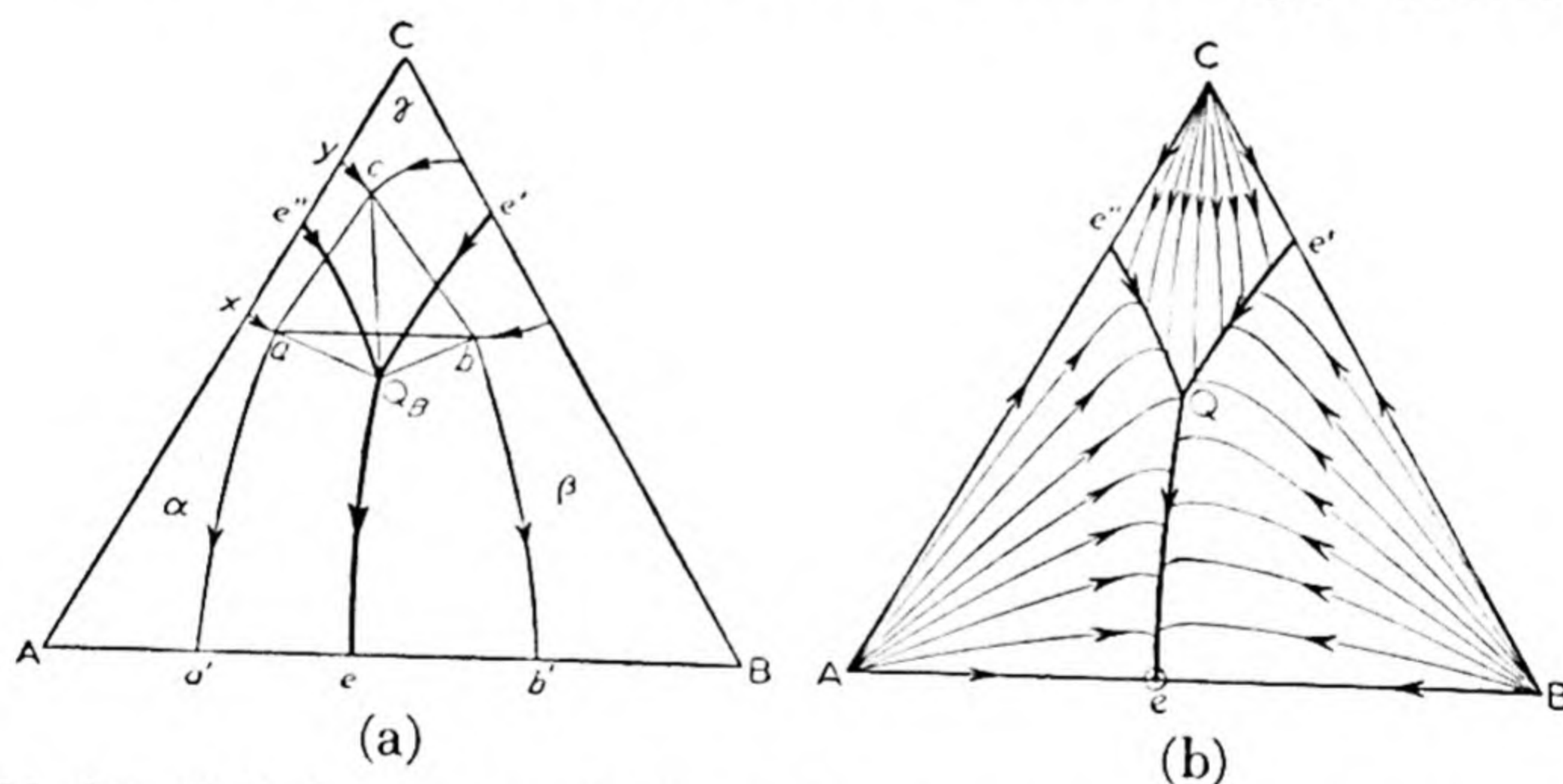


FIG. 11-29. Polythermal projection (a) and $Ph\ 2$ surface (b) of Fig. 11-28.

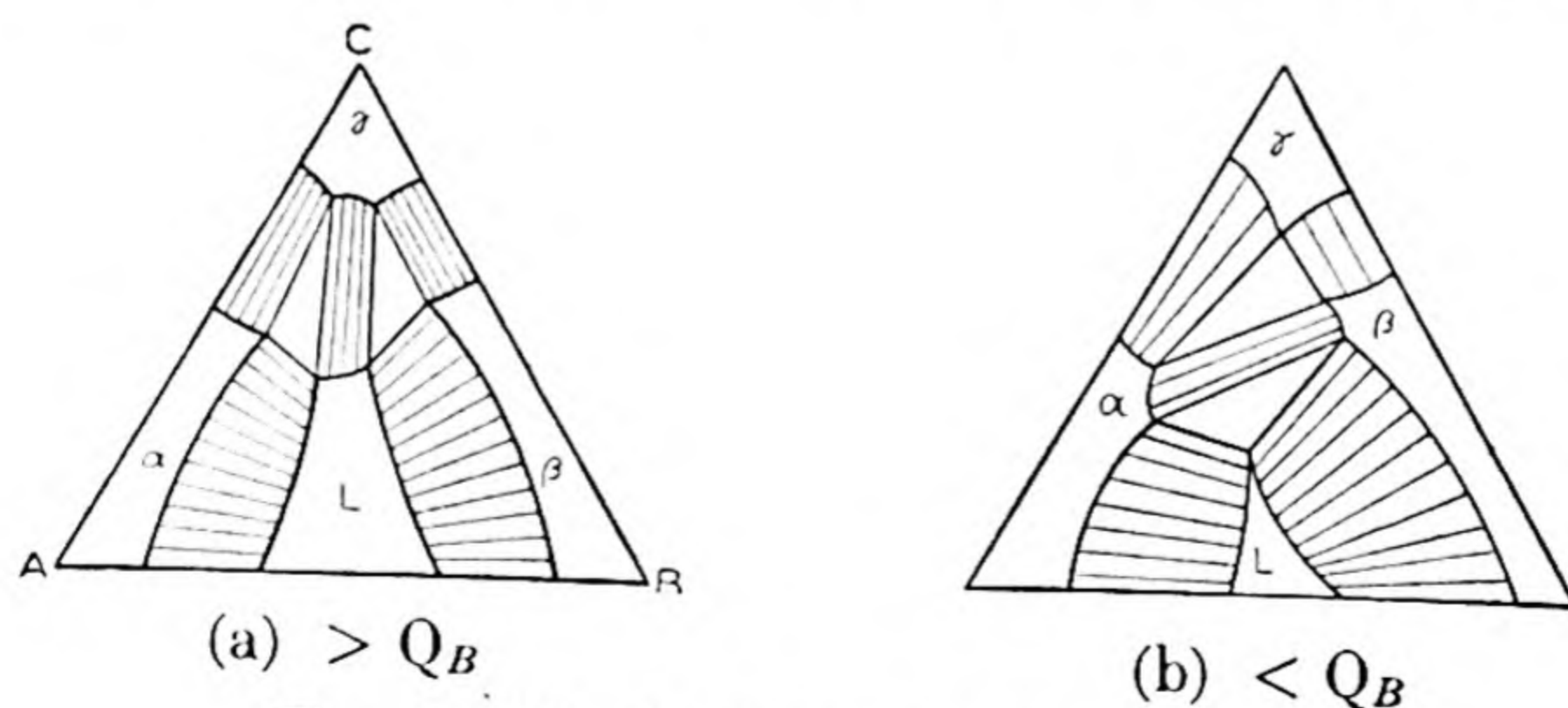


FIG. 11-30. Isotherms of Fig. 11-28.

pletely to $\alpha + \gamma$, with compositions on the curves xa and yc respectively, before reaching Q_B . The invariant Q_B is reached only by liquids with original composition in the invariant quadrangle Q_Bacb . The reaction at Q_B is $L + c \rightleftharpoons a + b + \text{cals.}$ If the composition is in abc , L is consumed, leaving the three solids. If the composition is in abQ_B , solid c is consumed, and the liquid begins to follow the curve Q_Be . Finally, all liquids with original composition in $abb'a'$, reaching the curve Q_Be either directly or through Q_B , solidify completely on the curve, leaving a mixture of $\alpha + \beta$, with compositions, respectively, on the curves aa' and bb' . With "effective removal of solid" the crystallization end-point for all compositions is the binary eutectic e (Fig. 11-29(b)). But for equilibrium solidification, Q_B is a crystallization end-point for all compositions in the triangle abc , just as E of Fig. 11-21 is the crystallization end-point for compositions in the triangle abc of that figure. But whereas E is in the triangle of its solids, Q_B is not; the first, then, is a "congruent" crystallization end-point, the second "incongruent."

2. Two Binary Systems Eutectic (e in $A-C$, e' in $B-C$), the Third Peritectic (p in $A-B$)

We shall take $e < e'$. If $p > e'$, the AB peritectic curve must fall in T in order to meet the curve from e' to e , at a 4-phase, diagonal type of invariant point, Q_B (ternary peritectic). But if $p < e'$, as in Fig. 11-31, the

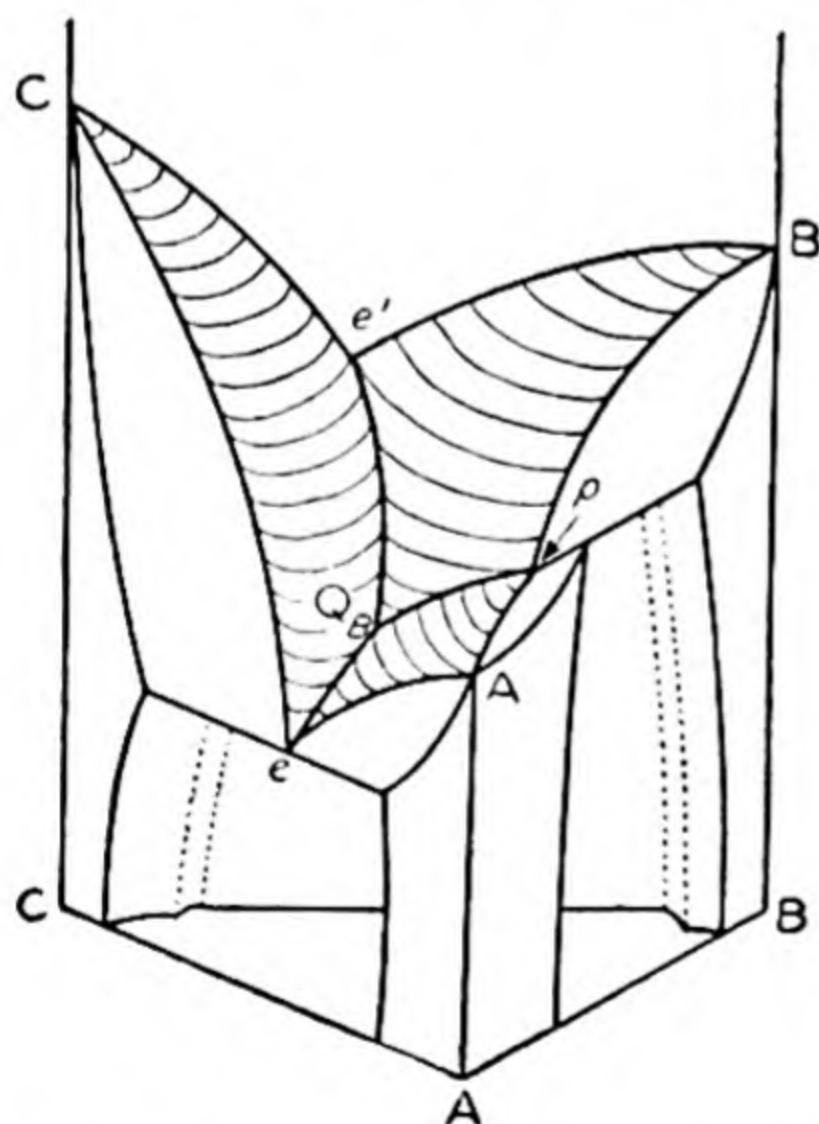


FIG. 11-31. Two binary eutectics and one peritectic.

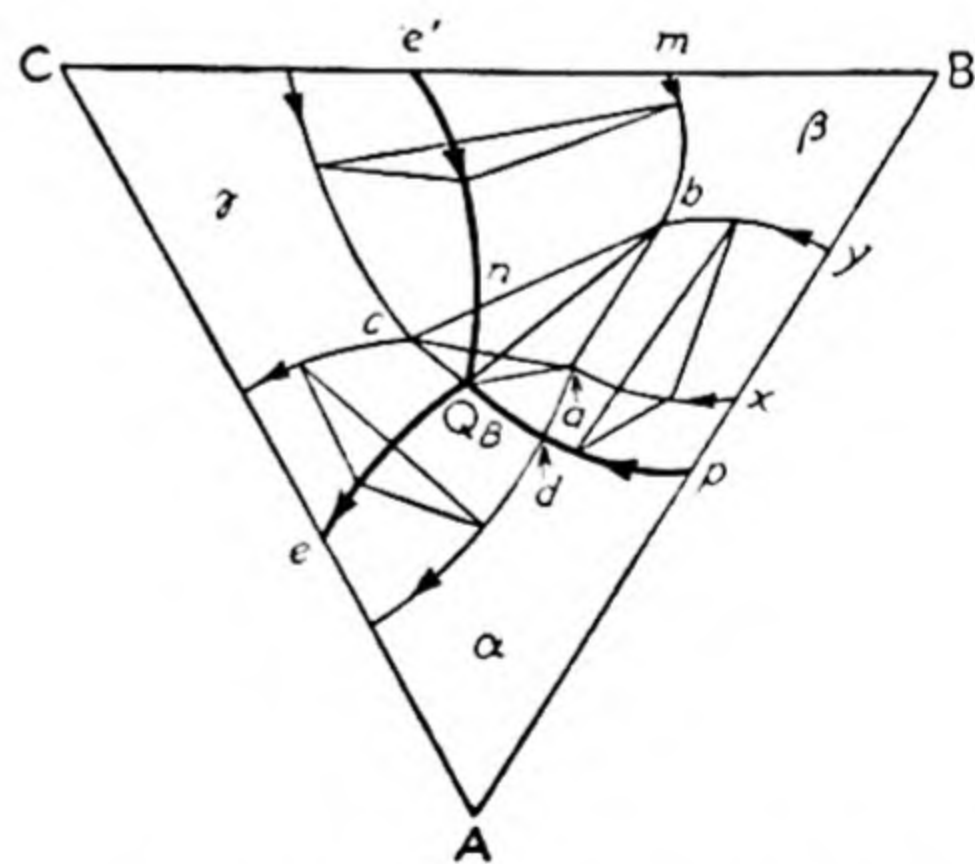


FIG. 11-32. Polythermal projection of Fig. 11-31.

peritectic curve may either fall or rise, and the ternary peritectic point will be either Q_B as before or Q_A , terminal for the α solid. In Fig. 11-31, then, the peritectic curve is assumed to fall in T from p to Q_B , and this may be the case whether p is $>$ or $< e'$. Two liquid curves of twofold saturation

therefore lead to Q_B from higher T : the liquid of the triangle $\gamma l\beta$ from e' and the liquid of the triangle $l\alpha\beta$ from p . These triangles meet at the temperature of Q_B to form the peritectic quadrangle $abcQ_B$ (the point Q_B being the liquid). At this point the reaction is $L + b \rightarrow a + c + \text{cals.}$

Any liquid with composition defined by the β crystallization surface (the β liquidus), $pQ_Be'B$ (Fig. 11-32), gives β solid in primary crystallization. This is the only process in its complete solidification, if the composition is in the field $Bybm$, or the β solidus. In $bme'nQ_B$, the liquid reaches the eutectic curve $e'Q_B$, and γ phase appears as second solid. During this secondary crystallization the liquid moves on curve $e'Q_B$ toward Q_B , but is consumed before reaching Q_B , leaving $\beta + \gamma$, unless the total composition is in the field nbQ_B . In the field pQ_Bby , α appears as second solid when the liquid reaches the peritectic curve pQ_B . The transformation of β to α now proceeds while the liquid moves on the curve toward Q_B , but again the liquid does not reach the invariant point unless the total composition is in Q_Bab . If it is in $abyx$, the liquid is consumed before Q_B is reached, leaving $\alpha + \beta$; if it is in pQ_Bax , β is consumed before the liquid reaches Q_B , leaving $L + \alpha$. When the liquid is no longer saturated with two solids, it leaves the curve pQ_B , moving away on the α liquidus (AeQ_Bp), while the composition of the saturating α phase changes. If P is in the α - γ MG , the liquid now reaches the curve Q_Be to solidify as a mixture of $\alpha + \gamma$; but otherwise, if P is in the region $pxad$, which is part of the α solidus, it does not reach the curve eQ_B since the solidification is completed to leave α phase as sole solid.

"Eutectic curves," such as $e'Q_B$ and eQ_B or, more generally, curves of even reaction, are approached during cooling by liquids from either side and are not left by these liquids during further cooling, except for unusual composition changes of saturating solid solutions as in Fig. 11-4(b). A "peritectic," transition curve or, strictly, an odd-reaction curve such as pQ_B , on the other hand, is reached from one side only, in the present case only by liquids with original compositions in the region pQ_Bby . It is left on the other side by liquids which lose the primary solid phase entirely while traveling on the curve. In this case the curve is left by all liquids with original compositions in the region pQ_Bax .

Q_B is reached only by liquids with original composition in the quadrangle $abcQ_B$. In abc , the liquid is consumed during the invariant reaction, leaving the 3-solid equilibrium, the course of which, as usual, is not shown in Fig. 11-32. In acQ_B , the b phase is consumed, and the system proceeds, univariantly, as T falls, along the set of curves from acQ_B to the AC eutectic, until liquid is consumed, leaving $\alpha + \gamma$. Q_B is therefore an incongruent crystallization end-point for compositions in abc .

The diagonal Q_Bb refers to the type of 3-phase univariant equilibrium

approaching Q_B from high T ; the diagonal ac , however, determines the type of equilibrium followed as T falls below Q_B (cf. Fig. 11-29). Further clarification will be obtained from the isotherms of Fig. 11-33, the order of

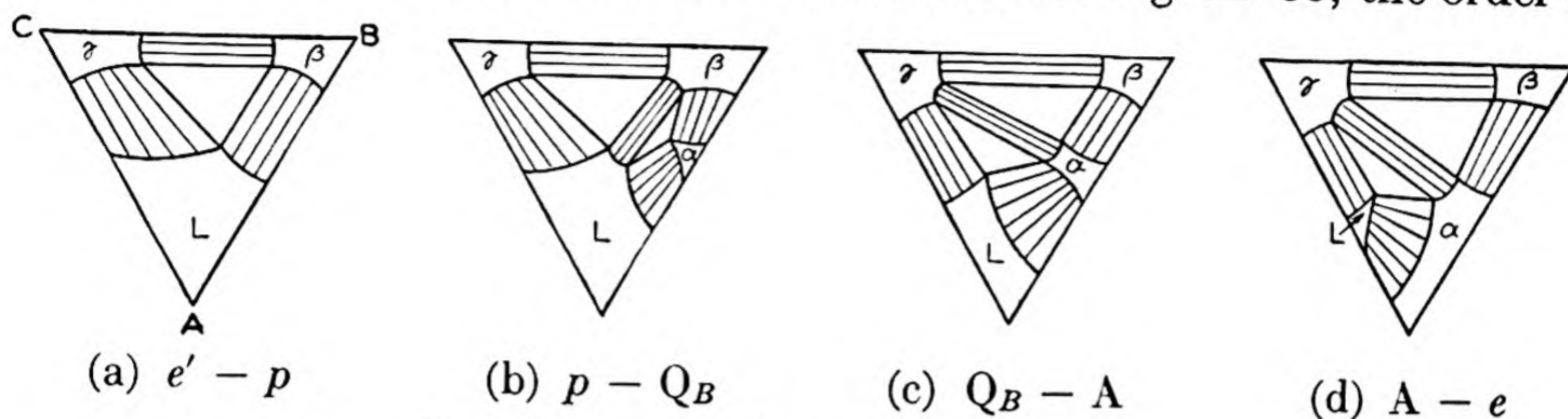


FIG. 11-33. Isotherms of Fig. 11-31.

T being assumed to be $e' > p > Q_B > A > e$. Below e the isotherm is the same as Fig. 11-22(e).

Finally, the crystallization paths for effective removal of solid during freezing appear as in Fig. 11-34.

If the peritectic curve rises as it enters the prism, Fig. 11-32 becomes Fig. 11-35. This figure shows the projections of three univariant systems,

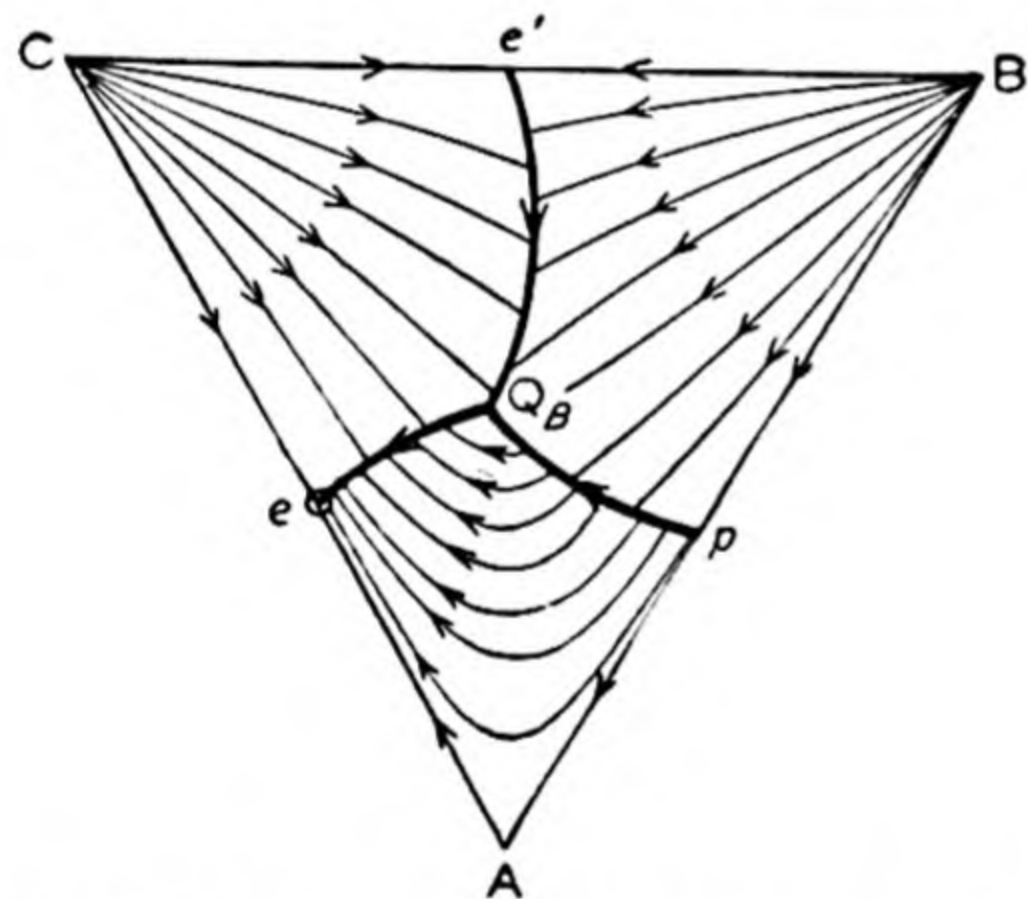


FIG. 11-34. Transition surface of Fig. 11-31.

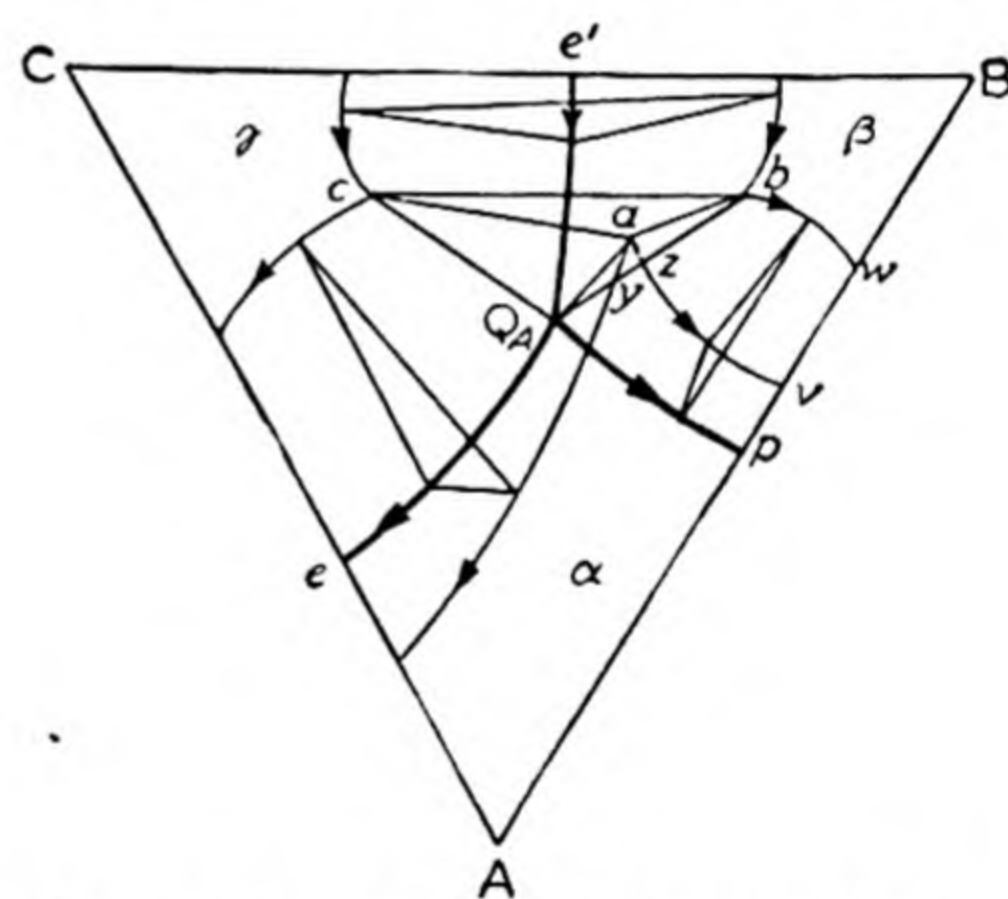


FIG. 11-35. Variation of Fig. 11-32, with $Q_A > p$.

involving L , meeting at the invariant Q_A . The even-type triangle $\gamma l\beta$ approaches from high T (the BC eutectic), becoming $cQ_A b$ at the invariant. The triangle $cQ_A a$ leaves the invariant as the system $\gamma l\alpha$, falling to the AC eutectic, and the triangle $Q_A ab$ leaves as $l\alpha\beta$, falling to the AB peritectic p . The triangle abc leaves, with falling T , as the 3-solid system $\alpha\beta\gamma$. The α phase therefore exists only below the temperature of Q_A . An isotherm just above Q_A would be similar to Fig. 11-33(a), while one just below Q_A is shown in Fig. 11-36. The α field, just appearing in Fig. 11-36 as T falls below Q_A , is comparable to the L field just appearing in Fig. 11-22(d) as T rises above E . The point Q_A is reached, on cooling, by liquids with original composition in cbQ_A , reaching Q_A on the curve $e'Q_A$. There they become

invariant during the reaction $L + c + b \rightarrow a + \text{cals.}$ If the composition is in caQ_A , b is consumed and the liquid follows curve Q_Ae ; in abQ_A , c is consumed, leading to curve Q_Ap . But in abc , the liquid is consumed, leaving the three solids. Q_A is therefore the incongruent crystallization end-point for compositions in abc . Liquids reaching Q_Ap , either from Q_A (triangle abQ_A) or from the β field on the pB side of Q_Ab , proceed toward p on the curve, with precipitation of α and solution of β , until, as in Fig. 11-32, liquid is consumed to leave $\alpha + \beta$, for original compositions in the α - β MG , $arwb$, or until β is consumed to leave $L + \alpha$, for compositions in the

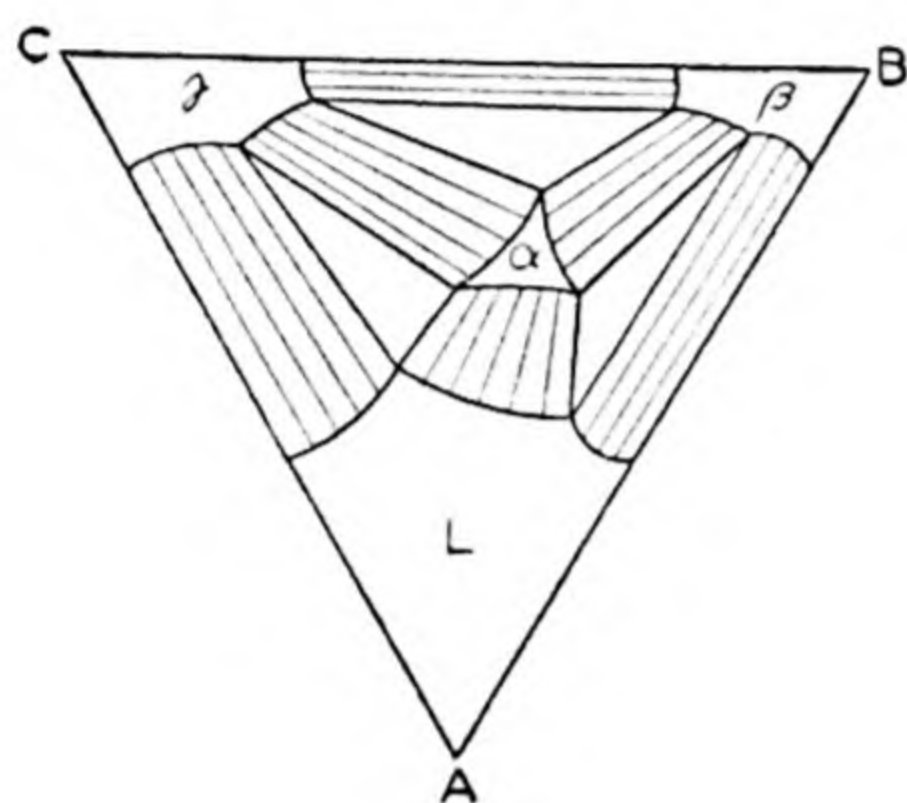


FIG. 11-36. Isotherm of Fig. 11-35, just below Q_A .

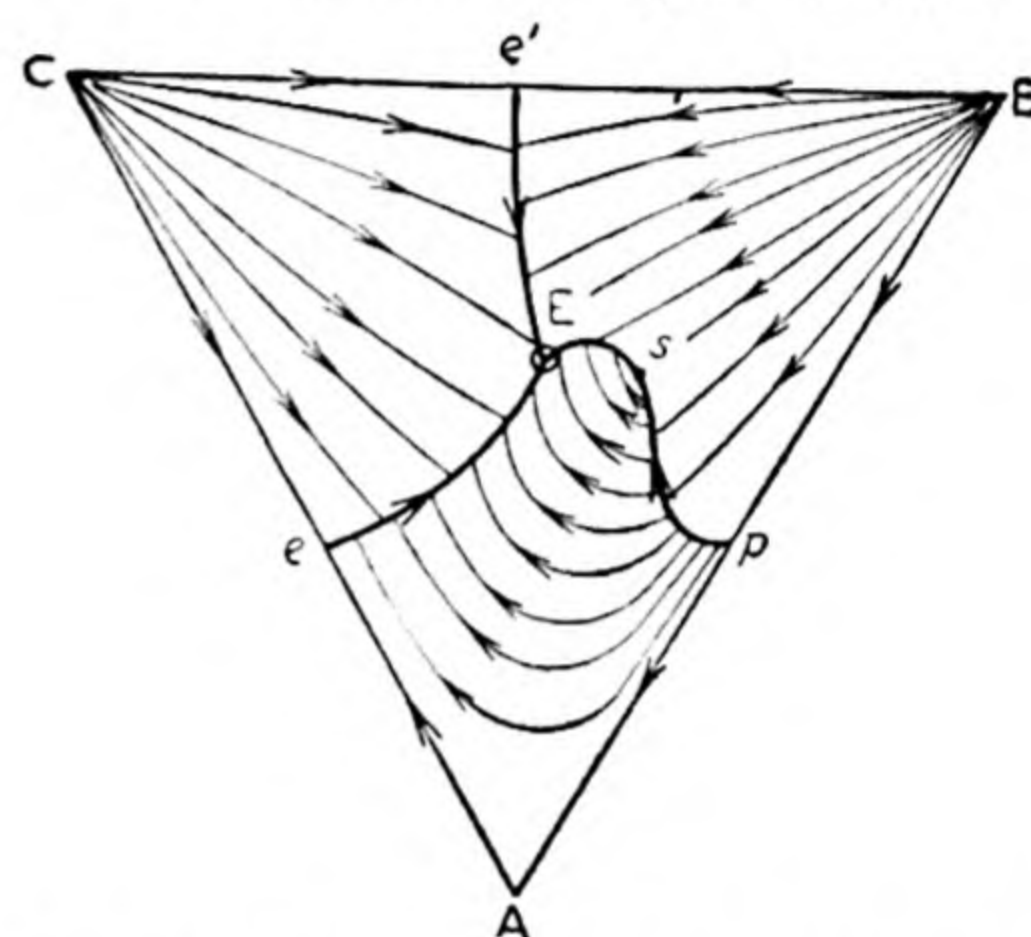


FIG. 11-37. Variation of Fig. 11-34, with change in reaction of the peritectic curve.

region $arpQ_A$. In the latter case the liquid leaves the curve and enters upon the α liquidus. Then if the original composition P is in the α solidus, the solidification is completed on the α liquidus; but if P is in the α - γ MG the liquid, carrying α , reaches the curve eQ_A and is consumed on that curve, to leave a mixture of $\alpha + \gamma$.

The phenomena for the region ayz , which is in the invariant triangle but also in the α solidus, are rather special. A liquid with this composition first precipitates β on cooling, since it falls in the β liquidus, and reaches the curve $e'Q_A$ to give the reaction $l \rightarrow \beta + \gamma + \text{cals.}$ When Q_A is reached, the solid a (α phase) appears and c (γ) is consumed. Then the liquid, saturated with α and β , travels along the peritectic curve Q_Ap until β is consumed, and then crosses into the α liquidus. It does not reach the curve Q_Ae , however, for it solidifies to the single α phase, with composition P in ayz .

The crystallization paths are still of the same general form as in Fig. 11-34, except for the change of direction on curve Q_Bp .

If the (odd) peritectic curve originating at p of Fig. 11-31 becomes even in reaction at some point s , before it intersects the curves from e and e' , the invariant point may be a ternary eutectic below all three binary invariants, and the crystallization paths would appear as in Fig. 11-37. Point s is explained under Fig. 11-19(b).

3. One Binary System Eutectic (e in $A-C$); Two Peritectic (p in $A-B$, p' in $B-C$)

If the peritectic curves become even in reaction as they enter the prism, at the points s, s , we may again have a ternary eutectic, as implied in the crystallization paths of Fig. 11-38, for various relations of the melting

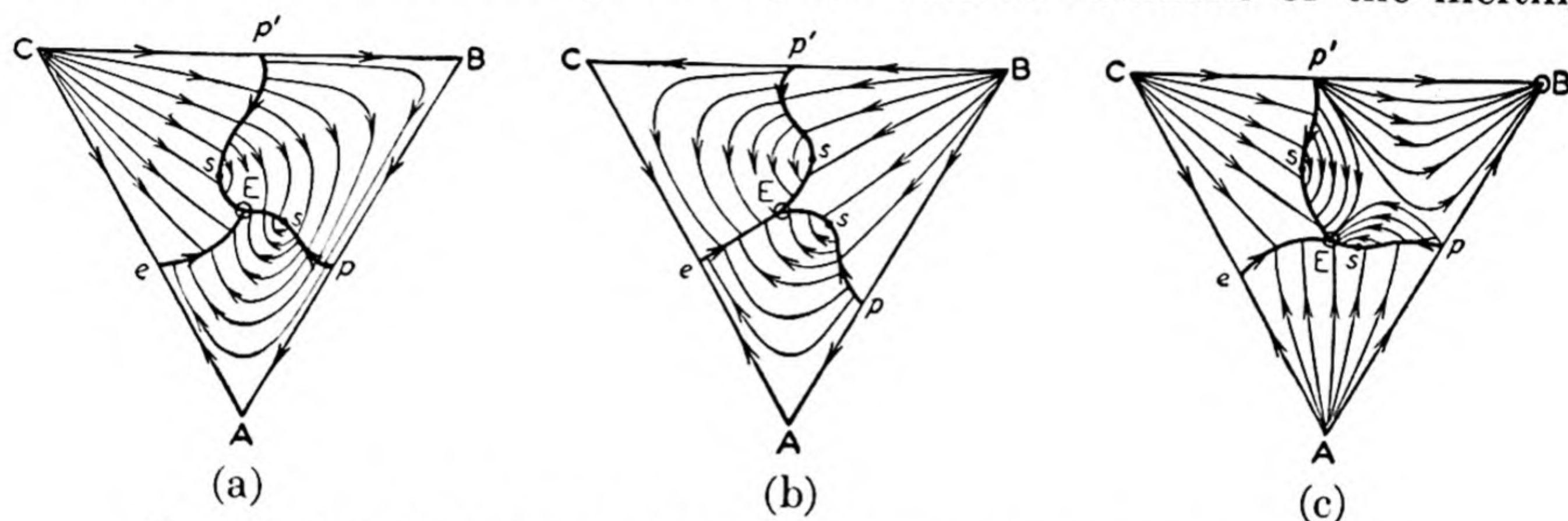


FIG. 11-38. Variations of Fig. 11-37, with two binary peritectics.

points involved, the three possibilities, with $C > A$, being (a) $C > B > A$, (b) $B > C > A$, and (c) $C > A > B$. In 11-38(a) and (b) the ternary eutectic is the only crystallization end-point. But in (c) there will be a ridge of maximum temperature between p and p' , so that pure B is also a crystallization end-point.

4. All Three Binary Systems Peritectic

If the peritectic curves of the preceding systems do not both become even before intersection, then no eutectic is possible, but only a variety of ternary peritectic points of both types (A and B). As an illustration for these cases as well as for the general case of three peritectic curves, we shall consider an example in which the invariant (type A) is the intersection of one peritectic curve from high T and two from below (Figs. 11-39 and 11-40). The essential difference between Fig. 11-40 and Fig. 11-35 is that the $\gamma\beta l$ and the $\gamma\alpha l$ triangles are now odd instead of even in reaction, but in both cases the α phase, being the interior point a of the invariant plane, is found in stable equilibrium only below the temperature Q_A . In the crystallization paths of Fig. 11-41, pure A is seen to be the crystallization end-point. An isotherm above Q_A would be similar to Fig. 11-33(a) and one just below Q_A similar to Fig. 11-36; the only difference would be in the angles of the 3-phase triangle $\gamma\alpha l$.

For equilibrium solidification the primary crystallization is determined (Fig. 11-40) by the liquidus fields $Ap_1Q_Ap_2$ for α , $p_1Bp_3Q_A$ for β and $p_3Cp_2Q_A$ for γ . In the γ field the curve p_3Q_A is reached only if the composition is in mp_3Q_{Ac} , and the curve Q_Ap_2 for the region xcQ_Ap_2 . If the curve p_3Q_A is

reached, the liquid does not reach Q_A unless the composition is in the triangle cbQ_A . Liquids with compositions in the $MG\ mnbc$ solidify to leave $\gamma + \beta$, while those in the region np_3Q_Ab have the γ phase consumed and cross into the β field. These then solidify on the β liquidus to leave β as

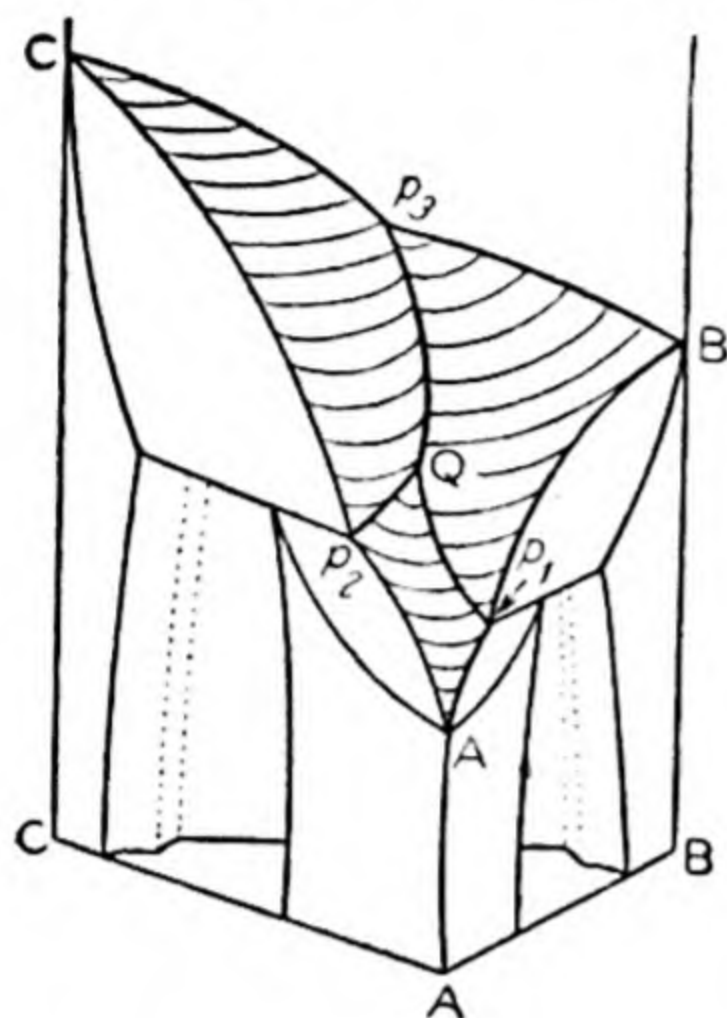


FIG. 11-39. Three binary peritectics.

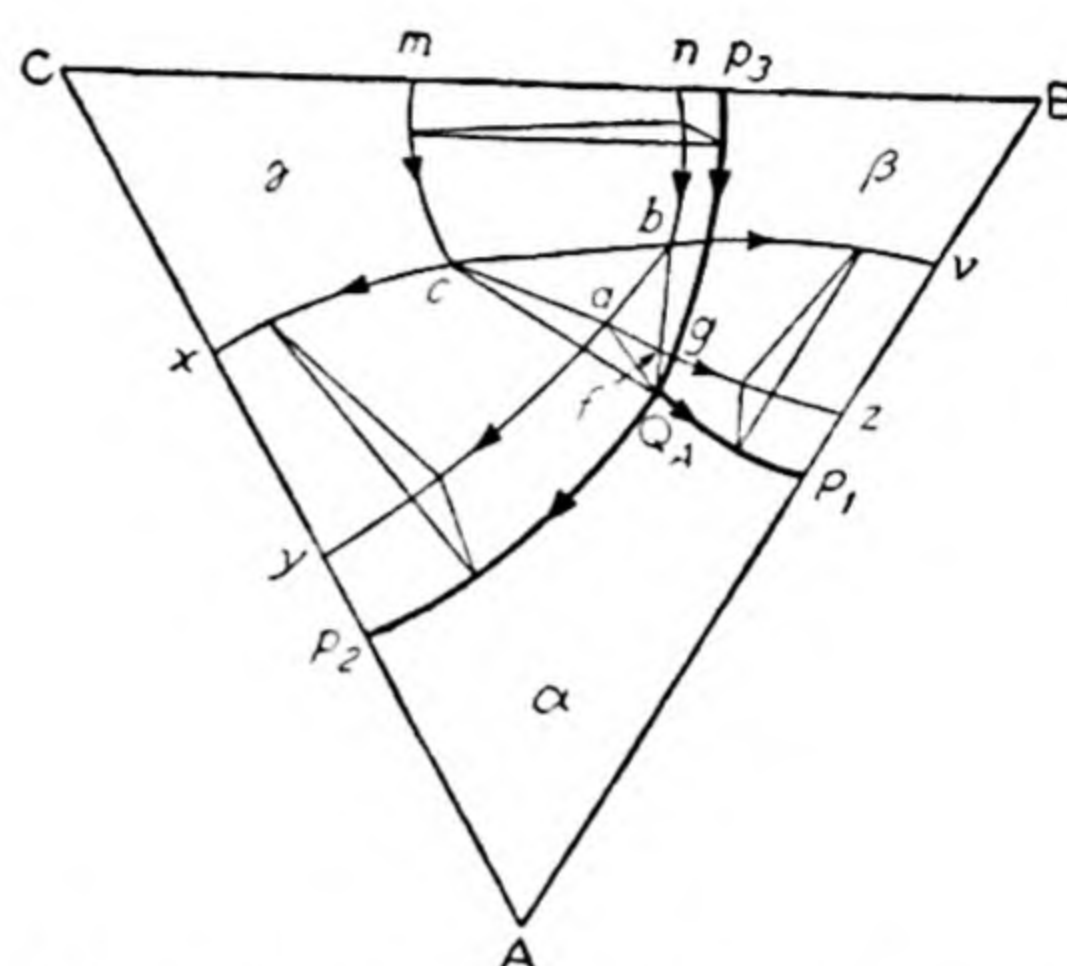


FIG. 11-40. Polythermal projection of Fig. 11-39.

sole solid, if the original composition P falls in the β solidus, $Bnbv$. The others reach the curve Q_Ap_1 where β begins to be transformed to α . Now if P is in the α - β MG , or vbQ_Ap_1 , the liquid is consumed on the curve, to leave $\alpha + \beta$; but if P is in the α solidus, $zayA$, β is consumed, the liquid leaves the curve and it completes its solidification on the α liquidus.

Liquids with original compositions in the triangle cbQ_A reach Q_A and are invariant during the peritectic reaction $L + c + b \rightarrow a + \text{cals}$. Those in abc , as usual, solidify completely, with Q_A as the incongruent crystallization end-point. Those in abQ_A enter the curve Q_Ap_1 , when c is consumed; those in caQ_A enter the curve Q_Ap_2 when b is consumed. Liquids reaching the curve Q_Ap_1 dissolve β and precipitate α as they cool. If the original composition is in the α - β gap, the liquid is consumed while still on the curve; otherwise β is consumed and the liquid crosses the curve into the α field, to solidify to α , with composition in the field azp_1Q_A . Similarly the liquids reaching curve Q_Ap_2 dissolve γ and precipitate α on cooling, and again if the original composition is in the region yaQ_Ap_2 the curve is crossed when γ is consumed, and the liquid finally solidifies to leave α alone, while if P is in the α - γ MG the liquid is consumed while still on the curve Q_Ap_2 . A liquid

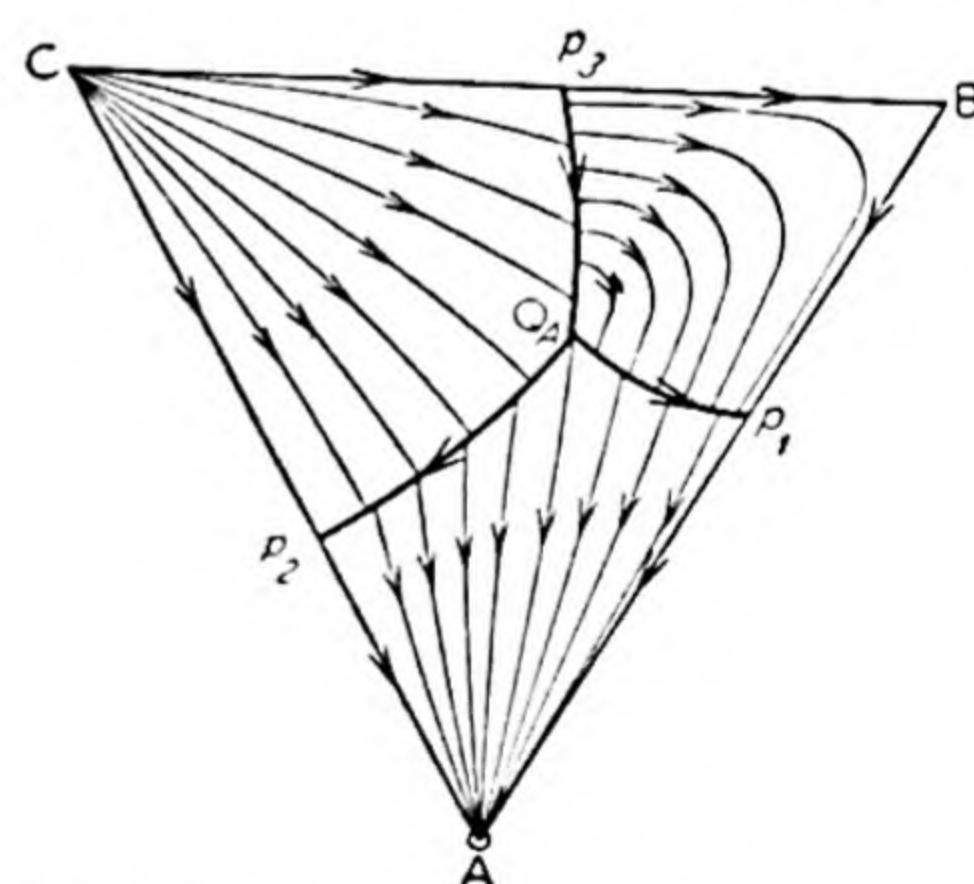


FIG. 11-41. Crystallization paths for Fig. 11-39.

in the small region fgQ_A therefore gives the following sequence of solid phases with complete equilibrium during solidification: γ , $\gamma + \beta$, β , $\beta + \alpha$, α . A liquid in the region afQ_A gives the sequence γ , $\gamma + \beta$, $\gamma + \beta + \alpha$, $\beta + \alpha$, α .

D. Miscibility Gap in One Binary System Only

If the gap in the system A–B does not extend across to another binary system at the freezing point surface of the ternary system, then the solid solution in equilibrium with liquid, or the solidus surface, is continuous around this gap. The equilibrium α/β , originating on the AB side, is therefore terminated, in this case, not at a 4-phase invariant nor at another binary invariant, but at a critical solution point where the α and β solid phases become identical ($=K'$) while in equilibrium with liquid ($=K$), the composition of which, of course, differs from that of the solid ($\alpha = \beta$) at point K' . This will be a singular "point" or equilibrium (at constant pressure), a system of three phases with an identity restriction.

1. Eutectic Case

We shall first consider the simplest possible case. The system A–B is **symmetrical** (optical isomers); its miscibility gap is therefore eutectic; C is an inactive substance completely miscible with both A and B in the

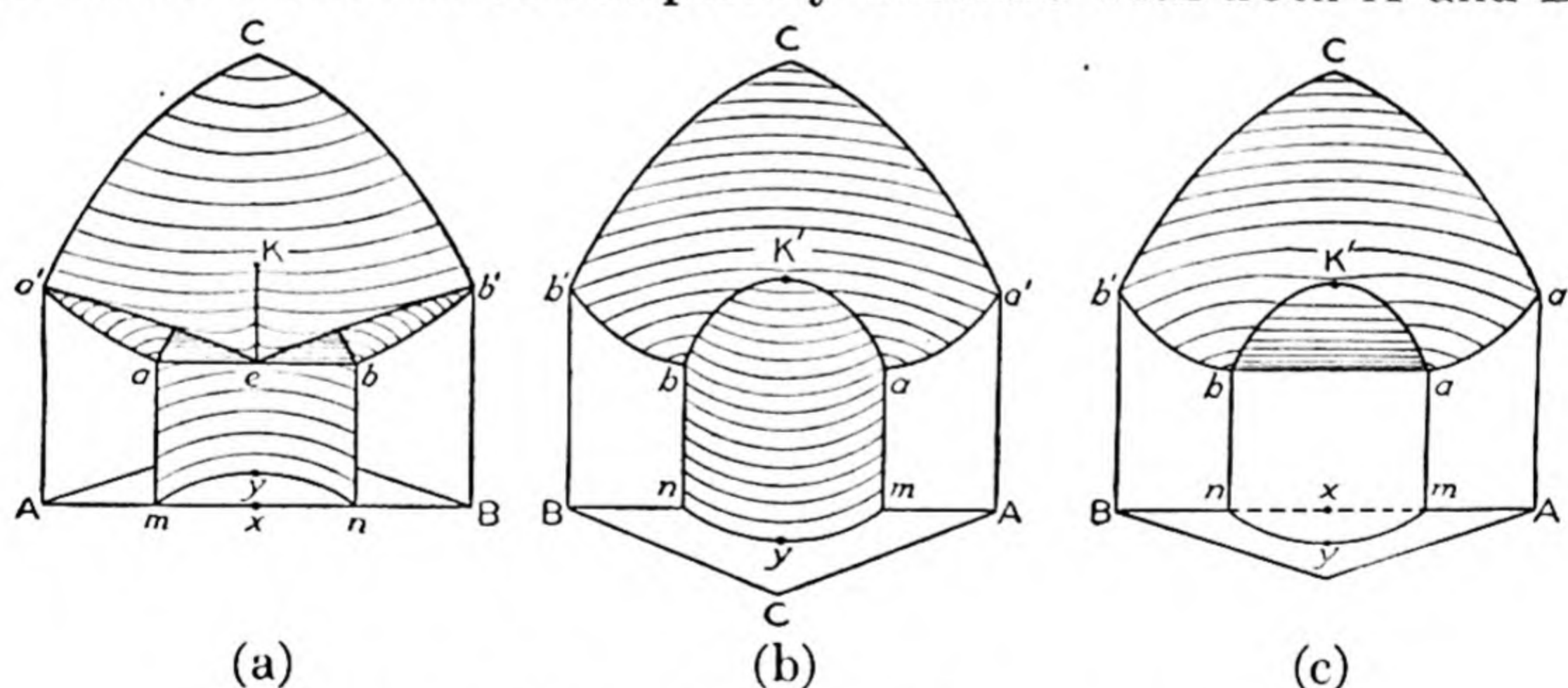


FIG. 11-42. MG in only one binary system (AB).

solid (and liquid) state, and its melting point is so high that the eutectic curve α/β rises in T from the AB side, as it enters the T/c prism (Figs. 11-42 to 11-45). The 3-phase triangle consequently has the configuration shown in Fig. 11-44.

In Fig. 11-42(a) the T/c prism is viewed from the AB side and from high T . The surface $a'eb'C$ is the liquidus, with a crease in it running from e to K , with increasing T . The solid MG , separating the phases α and β , is viewed, in its entirety, from the C side in Fig. 11-42(b). For simplicity we

are assuming the gap to be everywhere vertical, as seen in the section Cx of Fig. 11-43. Its course below its contact with the melting point surface has no bearing on the equilibria under discussion. The equilibrium of liquid with two solids starts at the binary eutectic line aeb , and rises in T as a

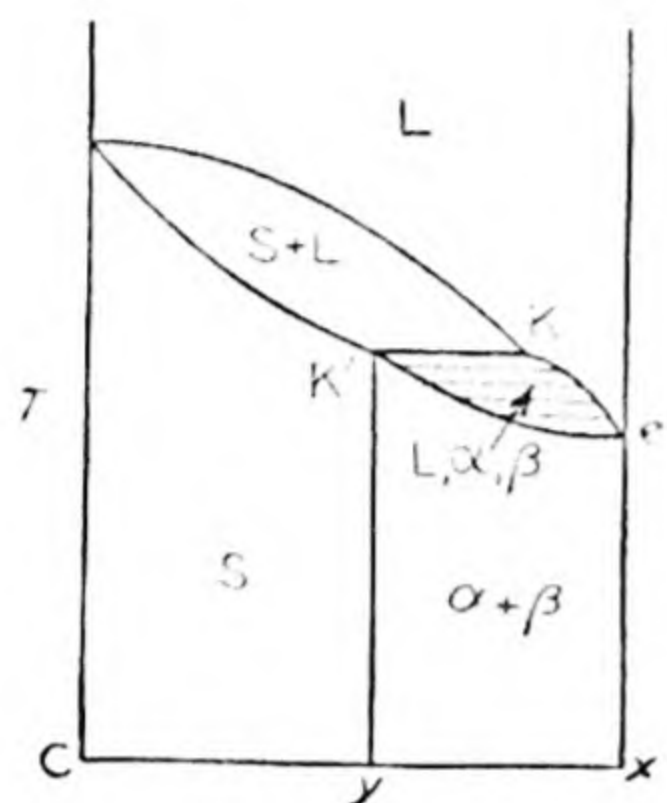


FIG. 11-43. Vertical section of Fig. 11-42, through C and *e*.

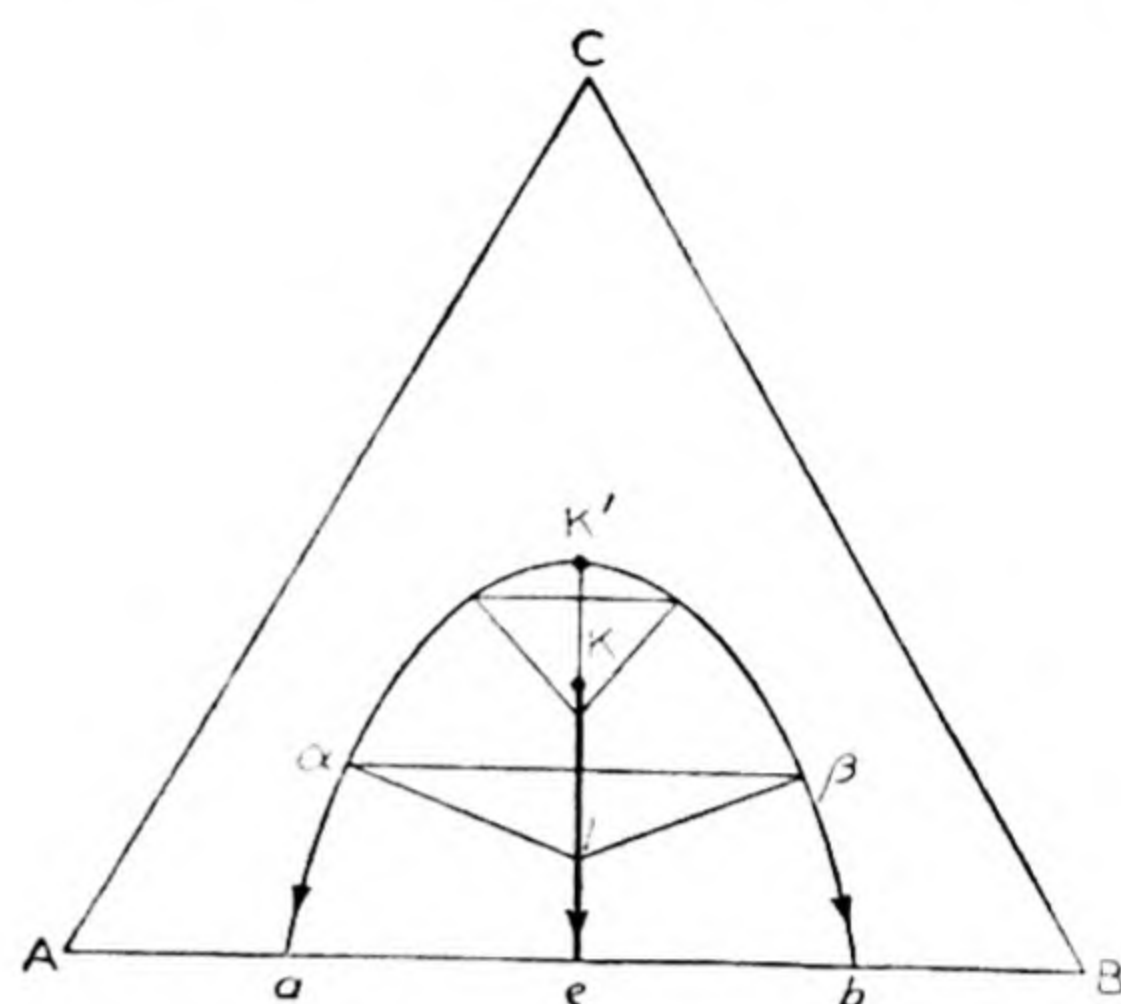


FIG. 11-44. Polythermal projection
of Fig. 11-42.

3-phase triangle $\alpha\beta$, projected in Fig. 11-44. The liquid describes the curve eK , while the base tie-line, $\alpha\beta$, describes the ruled surface abK' , viewed in part, in Fig. 11-42(a), and, and in its entirety, from the C side in Fig. 11-42(c), in which the wall of the MG has been removed. The two curves are also shown in the section (Fig. 11-43). The horizontal lines in Fig. 11-43

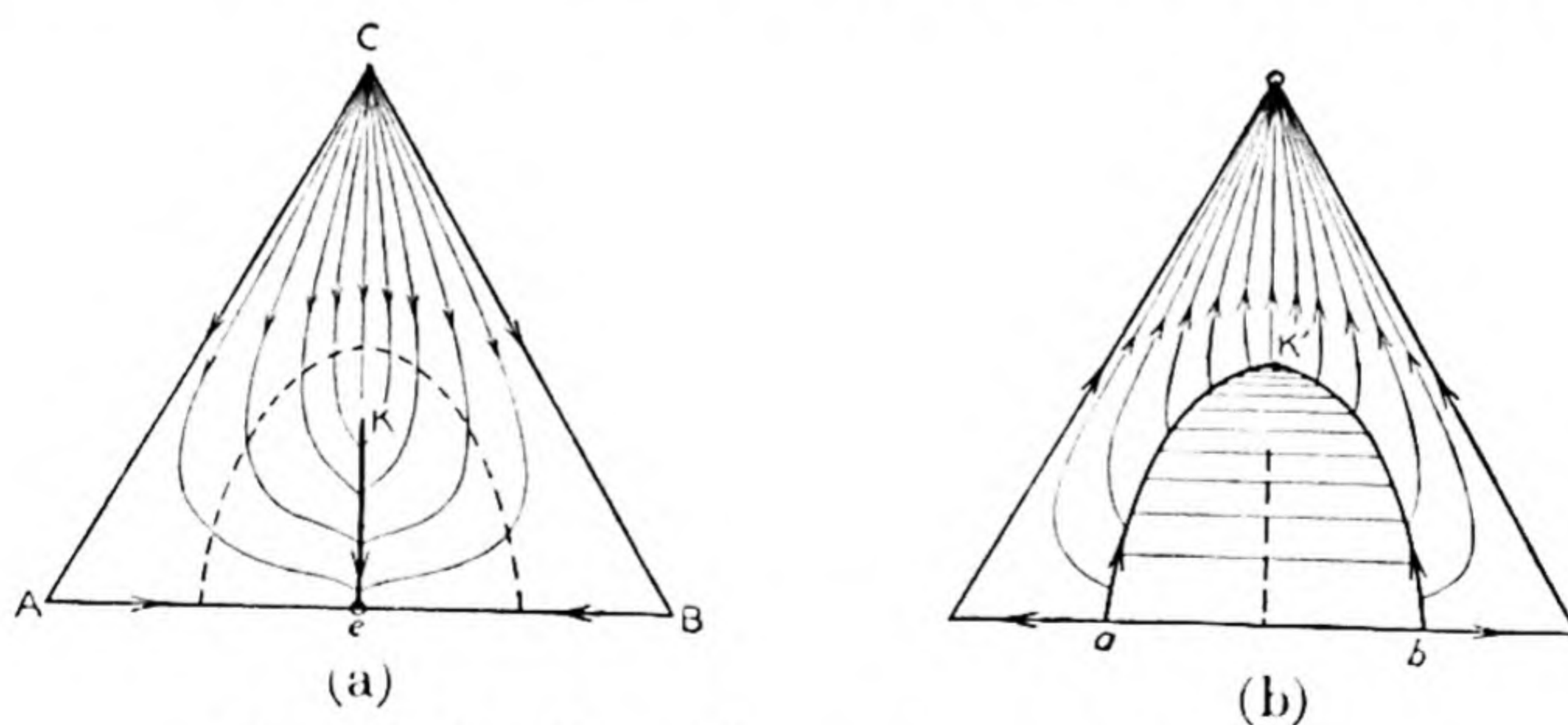


FIG. 11-45. Transition surfaces of Fig. 11-42.

are sections of the isothermal 3-phase triangles connecting liquid on eK with two solids, both superimposed on the curve eK' . The line KK' is the limiting triangle $\alpha\beta$ of Fig. 11-44, vanishing to a line when $\alpha = \beta$ at the critical solution point K, K' .

Fig. 11-46(a) is a vertical section parallel to AB, between C and K'; Fig. 11-46(b), between K' and K; and Fig. 11-46(c), between K and AB.

The region $L + \alpha + \beta$ of these sections is not bounded by sections of solubility surfaces, but by sections of the envelopes of the tie-lines of 3-phase triangles. The base fg itself is one of these tie-lines, such as $\alpha\beta$ of Fig. 11-44. The sides, such as lf and lg of Fig. 11-46(c), are points on the $l\alpha$ and

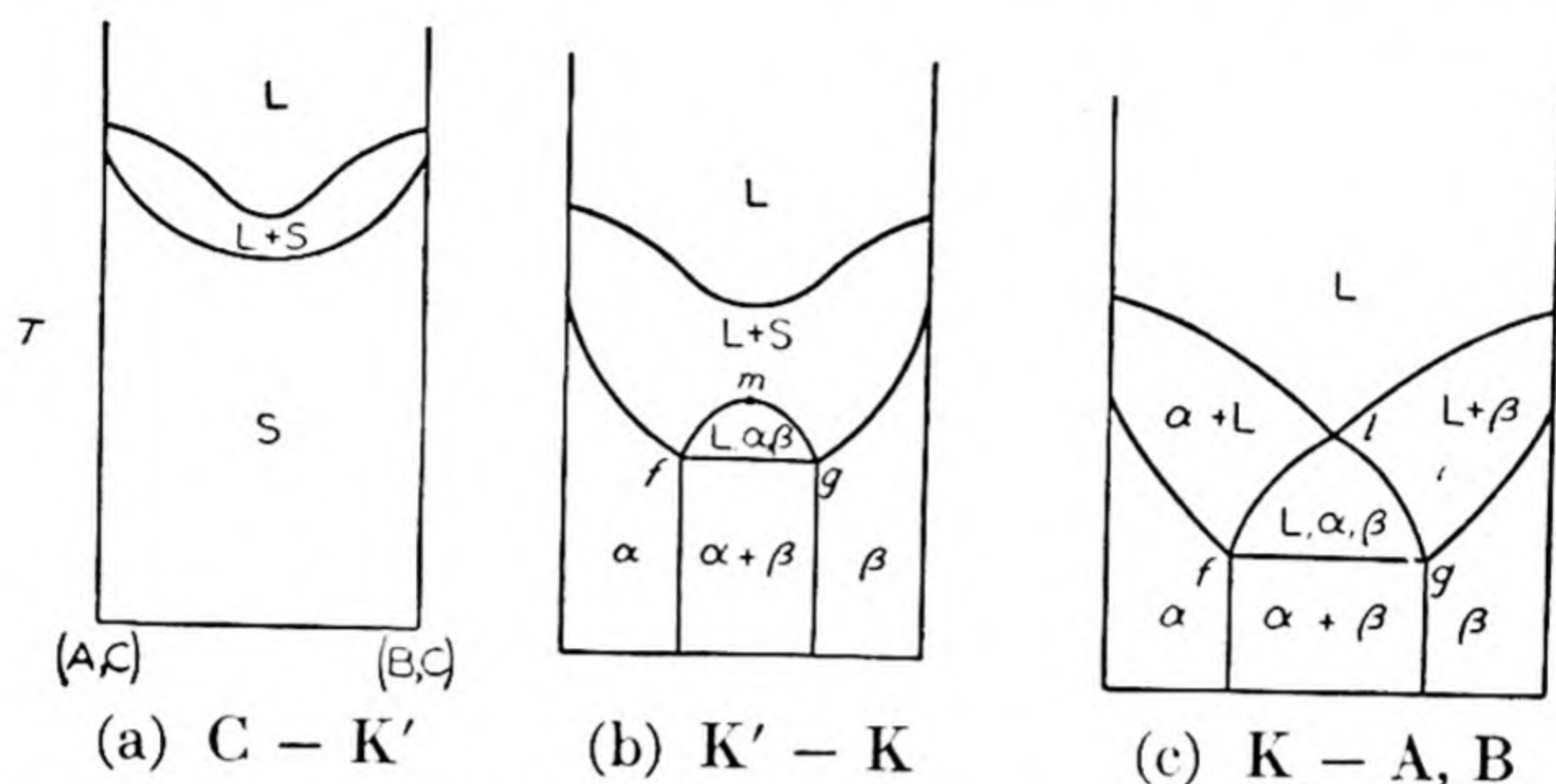


FIG. 11-46. Vertical sections of Fig. 11-42, parallel to AB.

$l\beta$ tie-lines of Fig. 11-44. The point m in 11-46(b) is on the KK' tie-line. Hence between K' and K this maximum of the $L + \alpha + \beta$ region of sections such as 11-46(b) remains constant, but the base falls in T from the K' section, where it starts as the point m itself, to the K section, where the liquidus surface first touches m . Between K and e , as in 11-46(c), both l and the

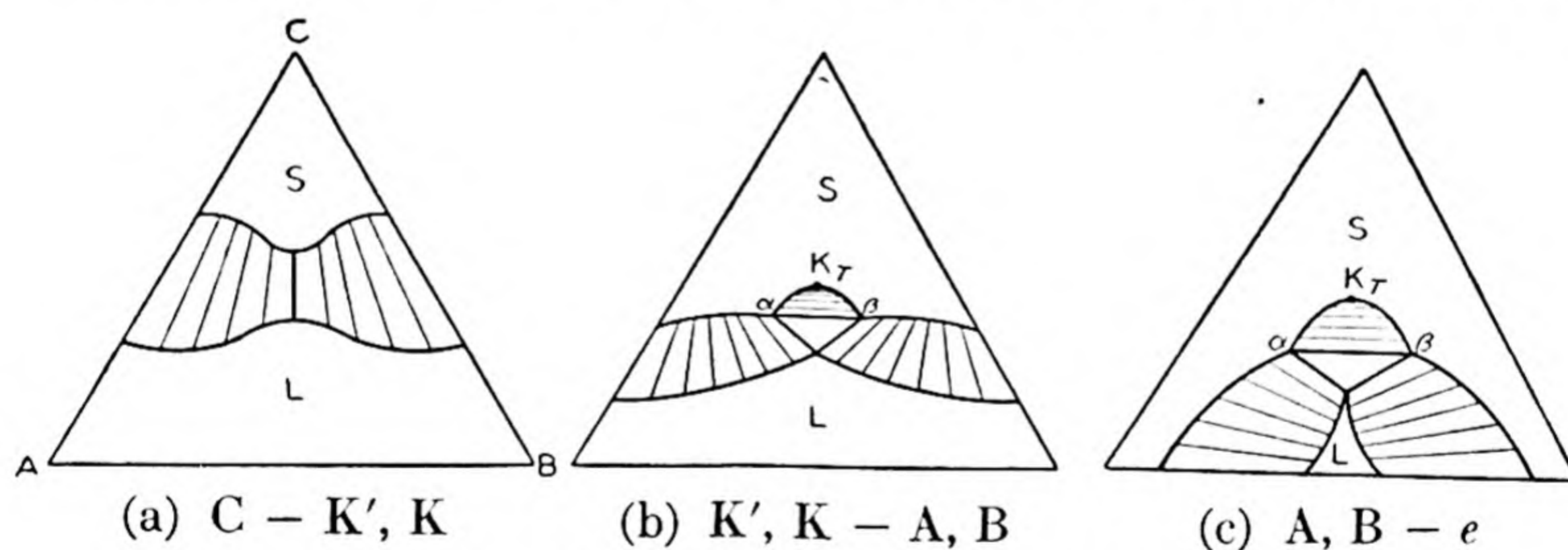


FIG. 11-47. Isotherms of Fig. 11-42.

base fg fall, with falling T , until they are isothermal at the binary eutectic.

All liquids outside the field $aK'b$ of Fig. 11-44 solidify completely without reaching any equilibrium involving two solids. As seen in Fig. 11-43, these liquids may extend into the field $aK'b$ before complete solidification, but the curve Ke is never reached. Only liquids with original composition in $aK'b$ reach this curve Ke . If the original composition is on the B side of $K'e$, the first solid is β phase, the second α . The liquid then moves along the curve toward e , but before this minimum is reached the liquid is consumed, leaving $\alpha + \beta$. The point K itself is reached only by liquids with original

composition on the line $K'K$. The crystallization paths for "effective removal" of solid are shown in Fig. 11-45(a), the boiling point paths in 11-45(b) which is to be compared with 11-9(b). During the boiling of the conjugate liquids of this ternary system, their compositions change, simultaneously, along the curves aK' and bK' , toward the point K' , while the vapor given off has a composition on the curve eK .

Fig. 11-47(a) is an isotherm just above the temperature K', K ; 11-47(b) between $K'K$ and the melting point of A and B; and 11-47(c) below the

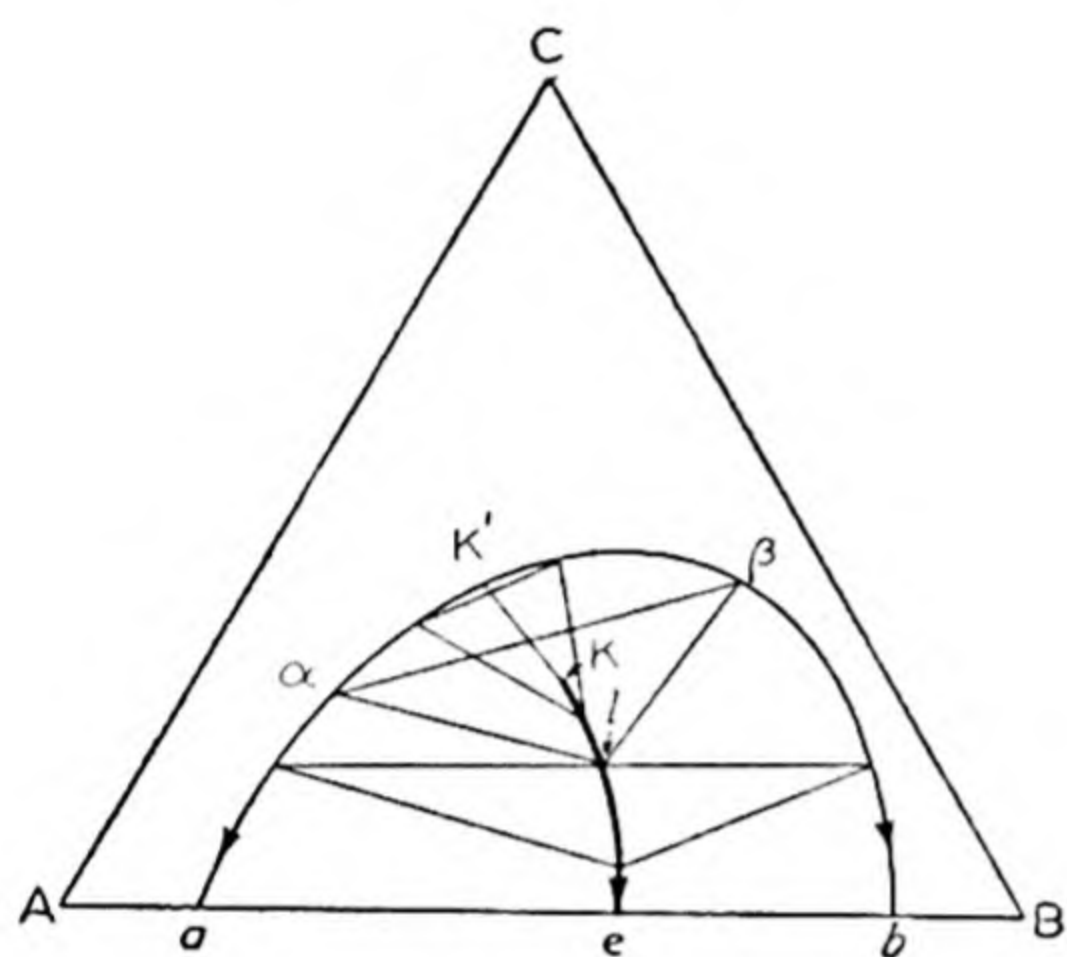


FIG. 11-48. System unsymmetrical, curve eK always even in reaction.

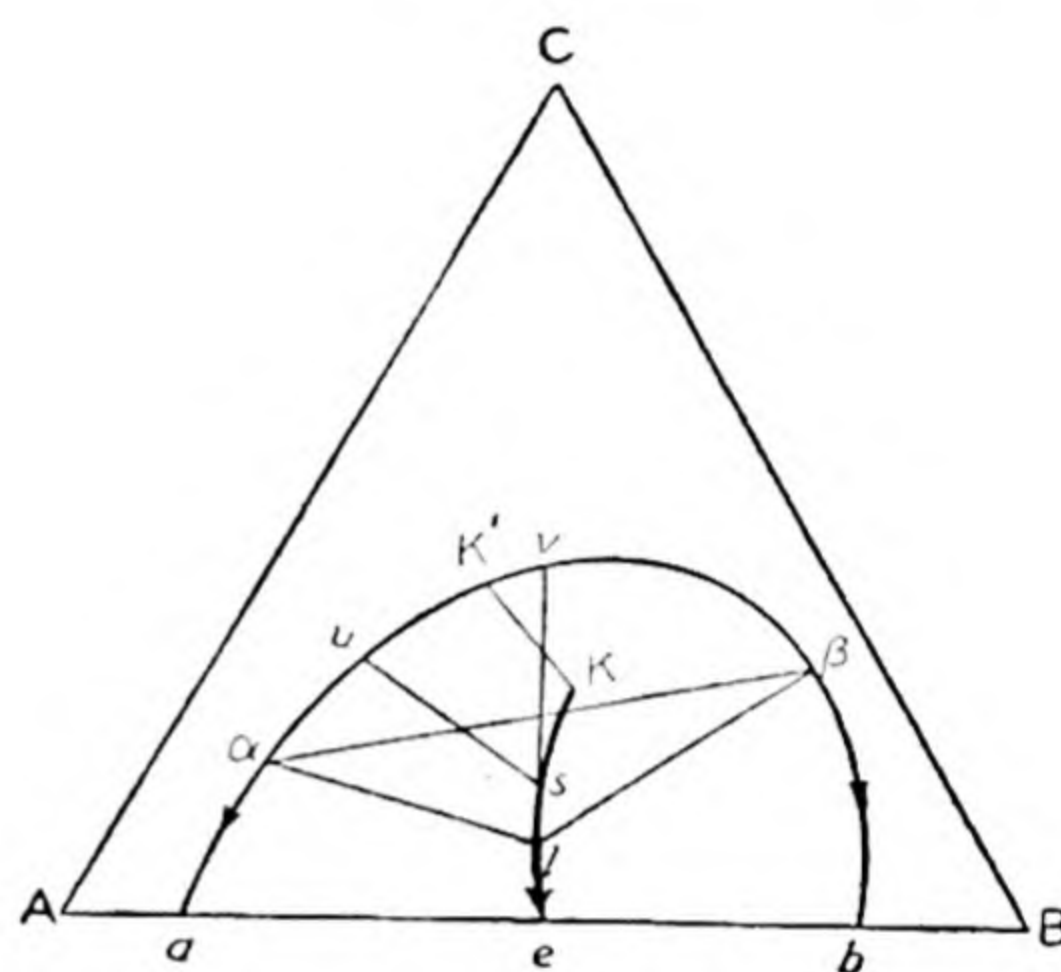


FIG. 11-49. Reaction of eK starts as odd at K (temperature falling from K to e).

latter temperature. K_T represents the critical solution point ($\alpha = \beta$) for the isotherm.

If the A-B system is **unsymmetrical**, the relations given still hold qualitatively so long as eK is of even reaction throughout. Fig. 11-44 becomes Fig. 11-48. Compositions on the right of $K'Ke$ but in $aK'b$ give β as first solid, and α as second when the liquid reaches eK .

For the curve eK to remain even in reaction up to point K , however, requires that its terminal tangent be the line KK' . In the unsymmetrical case, then, the curve will, in general, become odd in reaction at some point s , as in Fig. 11-49, while still rising in T from e to K . The $\alpha\beta$ triangle is even in reaction, starting from e , until the $l\beta$ side becomes tangent to the eK curve at s in the triangle usv . Between s and K , as u and v converge upon K' , the triangle is odd ($\alpha -$, $\beta +$).

Compositions on the β side of $K'Ke$ and in the MG again give β as first solid, and α as the second when the liquid reaches eK , the solidification proceeding normally. For those on the α side of $K'Ke$, it is necessary to consider the projection of the envelope generated by the $l\beta$ tie-lines between $K'K$ and vs , with falling T ; this projection is shown as a dotted curve in Fig. 11-50.

Compositions in the region $aK'se$ of Fig. 11-50 give α and then β , in a normal solidification process. Those in $K'Ks$, however, begin by precipitating α until the α and L phases reach, simultaneously, the curves uK' and sK , respectively, when β begins to form. At this point the total

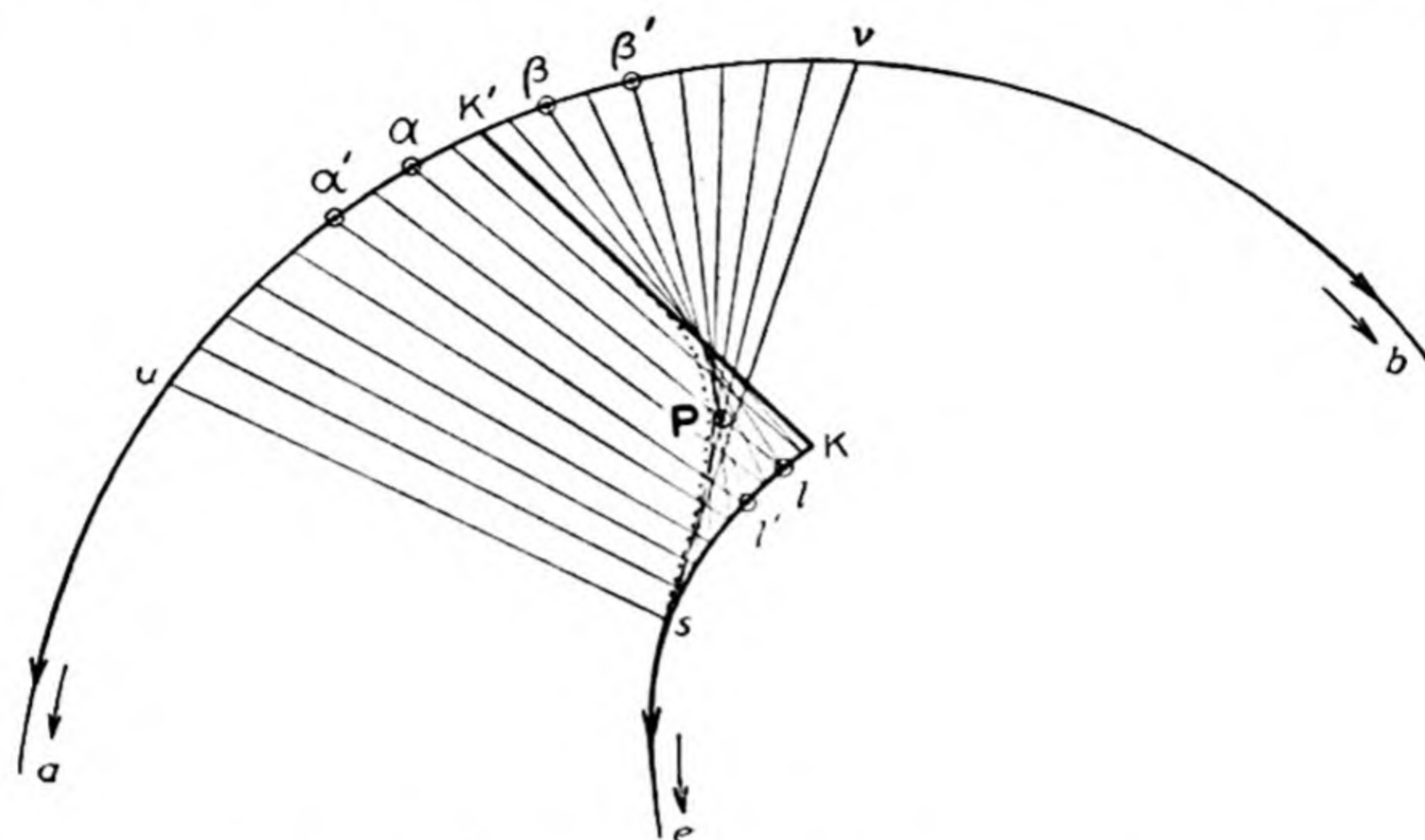


FIG. 11-50. Detail of Fig. 11-49.

composition, P , lies on an αl tie-line, and the β phase appears with the composition β . As T falls, β moves toward v , α toward u , l toward s , until, as explained in connection with Figs. 11-4(a, b), P lies on the tie-line $l'\beta'$ of the triangle $\alpha'\beta'l'$. At this point, then, the α phase (primary crystallization) will have vanished, leaving $l' + \beta'$. But since the final condition, with point P in the MG , must be a mixture of $\alpha + \beta$, the liquid returns again, at still lower T , after composition changes in both l and β , to the even section of the curve se , and finally disappears to leave $\alpha + \beta$.

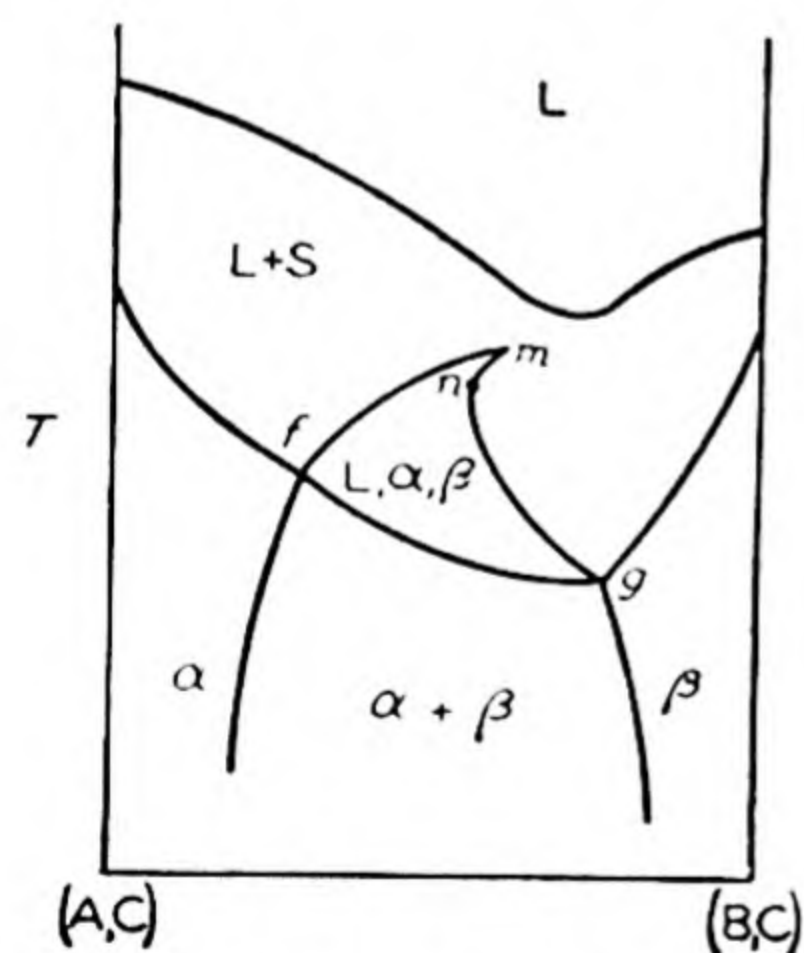


FIG. 11-51. Vertical section of Fig. 11-49, between K' and K .

For later reference we note that for compositions in the envelope region $KK's$ the sequence of solids in equilibrium solidification is α , $\alpha + \beta$, β , $\alpha + \beta$. In terms of the section of Fig. 11-46(b), which in the present unsymmetrical case becomes Fig. 11-51, between K' and K , we see that if the composition lies between m and n of Fig. 11-51, the $l + \alpha$ system precipitates β when its temperature falls below the curve fm , and becomes $l + \beta$ when it crosses the curve nm . Further cooling brings it again into the 3-phase equilibrium,

when a temperature on ng is reached, and finally, passing through fg , the liquid disappears, leaving $\alpha + \beta$. The crystallization paths for effective removal of solid are shown in Fig. 11-52(a) and the boiling point paths in 11-52(b).

An example of these relations is found in the freezing point diagram of the system $\text{Ag}(=\text{A})\text{--Cu}(=\text{B})\text{--Au}(=\text{C})$, with melting points of 961° , 1083° and 1063° respectively, and with the slight variation that there is a minimum in the freezing point temperatures of the continuous solid solution of the binary system Cu--Au .³

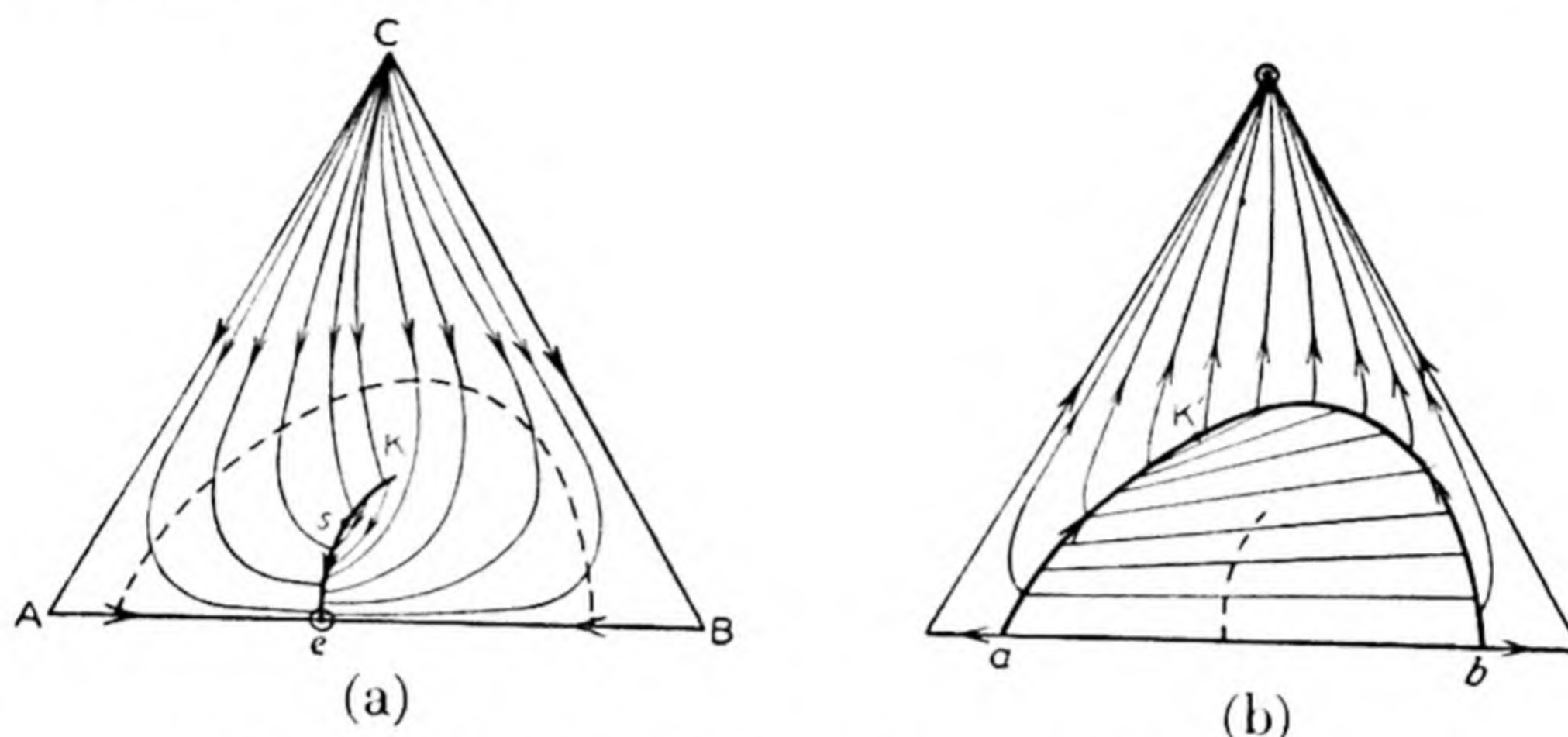


FIG. 11-52. Transition surfaces of Fig. 11-49.

The relations just discussed are qualitatively the same if the curvature of the polythermal projection of the curve Ke were the opposite of that assumed in Fig. 11-50; the corner K would simply lie on the left of the tie-line sv . The other curvature is illustrated later in Fig. 12-13.

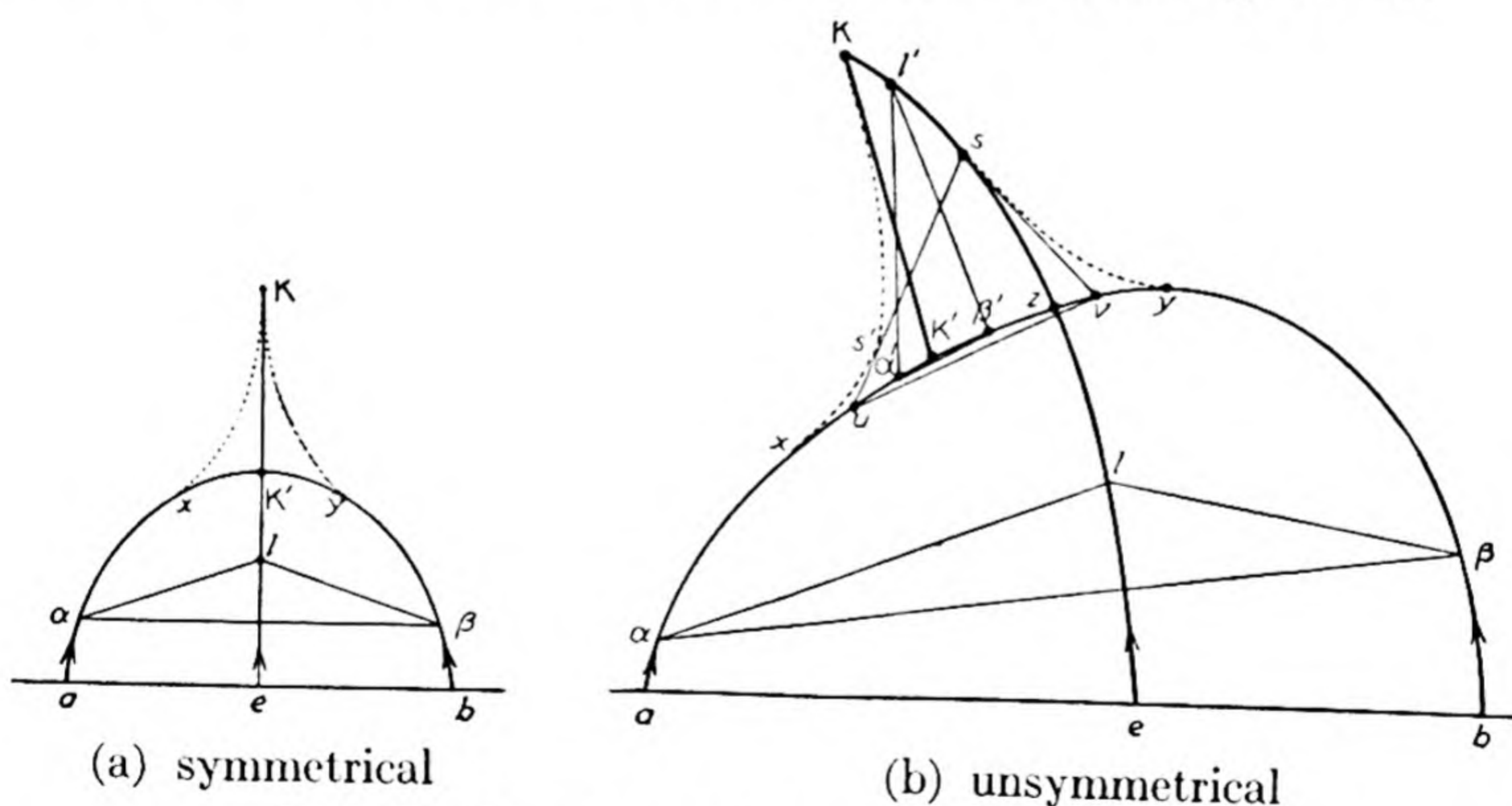


FIG. 11-53. Temperature falling from e to K .

If T falls from e to K , the A--B system still being eutectic, the projections 11-44 and 11-49 become Figs. 11-53(a) and (b) respectively.⁴ Now the melting point of C is $< \text{K} < e$. The section Ce for the symmetrical case

³ E. Jänecke, *Metallurgie*, 8, 597 (1921).

⁴ For discussion of the unsymmetrical case see also G. Masing (Ref. L), *Ternary Systems*, Chapter VIII.

is Fig. 11-54, and the crystallization paths for effective removal of solid for the unsymmetrical case are shown in Fig. 11-55; the boiling point paths would be as in 11-45(b) and 11-52(b), with reversed directions. Isotherms for the system of Fig. 11-53(b) are shown in Fig. 11-56, (a) between C and KK' , (b) between KK' and e .

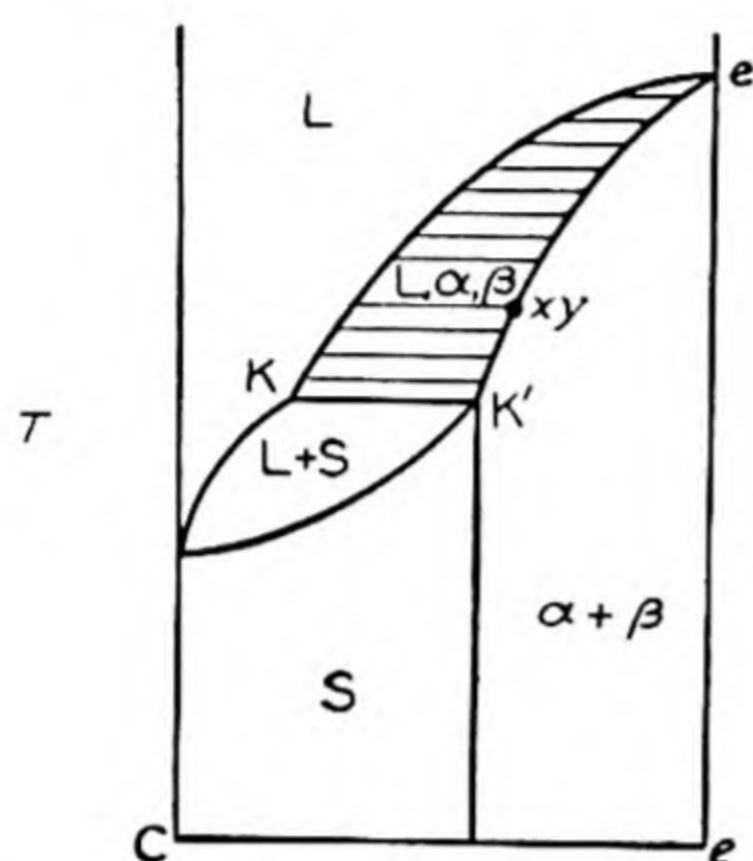


FIG. 11-54. Vertical section of Fig. 11-53 (a).

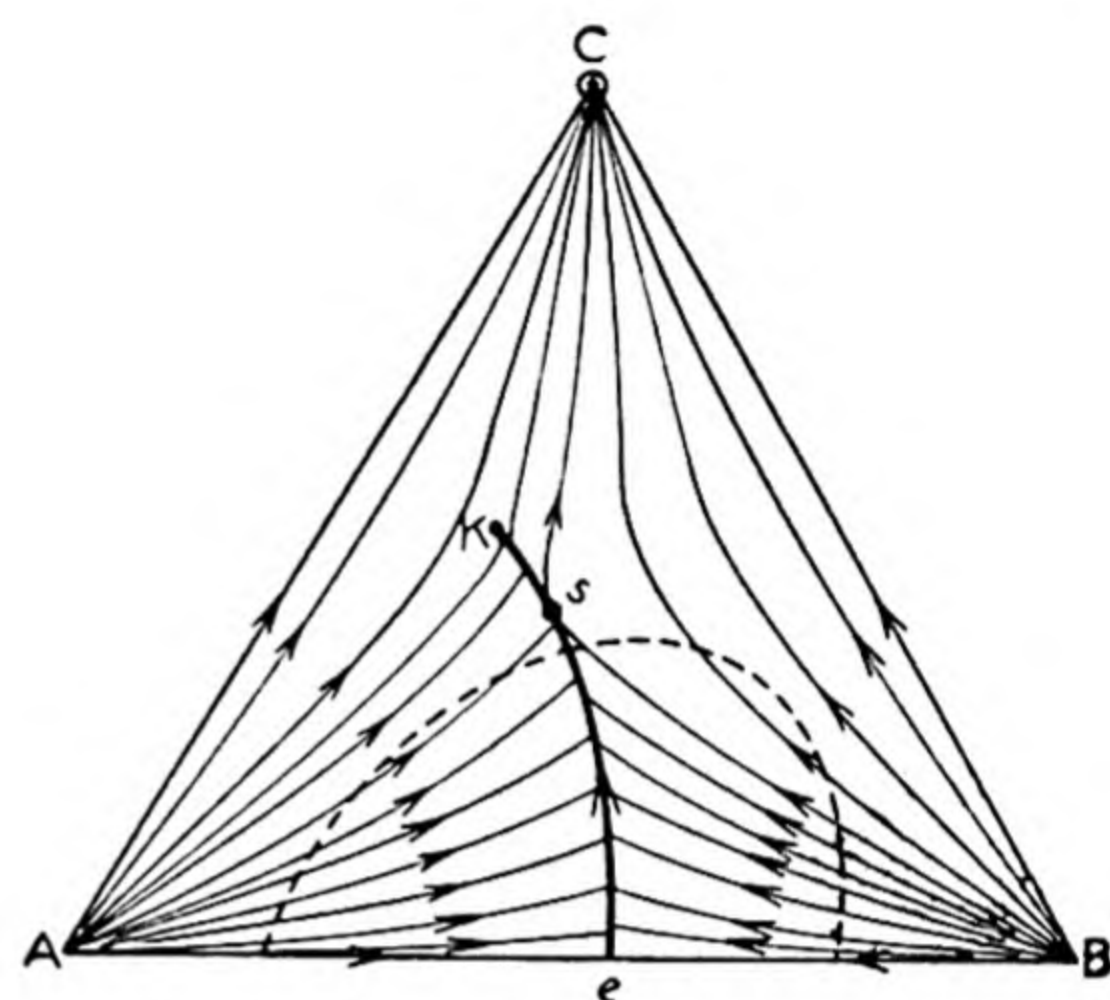


FIG. 11-55. Transition surface of Fig. 11-53(b).

In the unsymmetrical case (Fig. 53(b)), the 3-phase system $\alpha l\beta$ is shown becoming odd in reaction ($\alpha -$, $\beta +$) between s and K , the limiting triangle being su , with the $l\beta$ side tangent to the liquid curve eK at point s . Thus the triangle $\alpha l\beta$ is even on the section es while $\alpha'l'\beta'$ on the section sK is odd in reaction. Crystallization paths for effective removal of solid, as in Fig. 11-55, lead to the curve from both sides in its even section, es ; over its odd

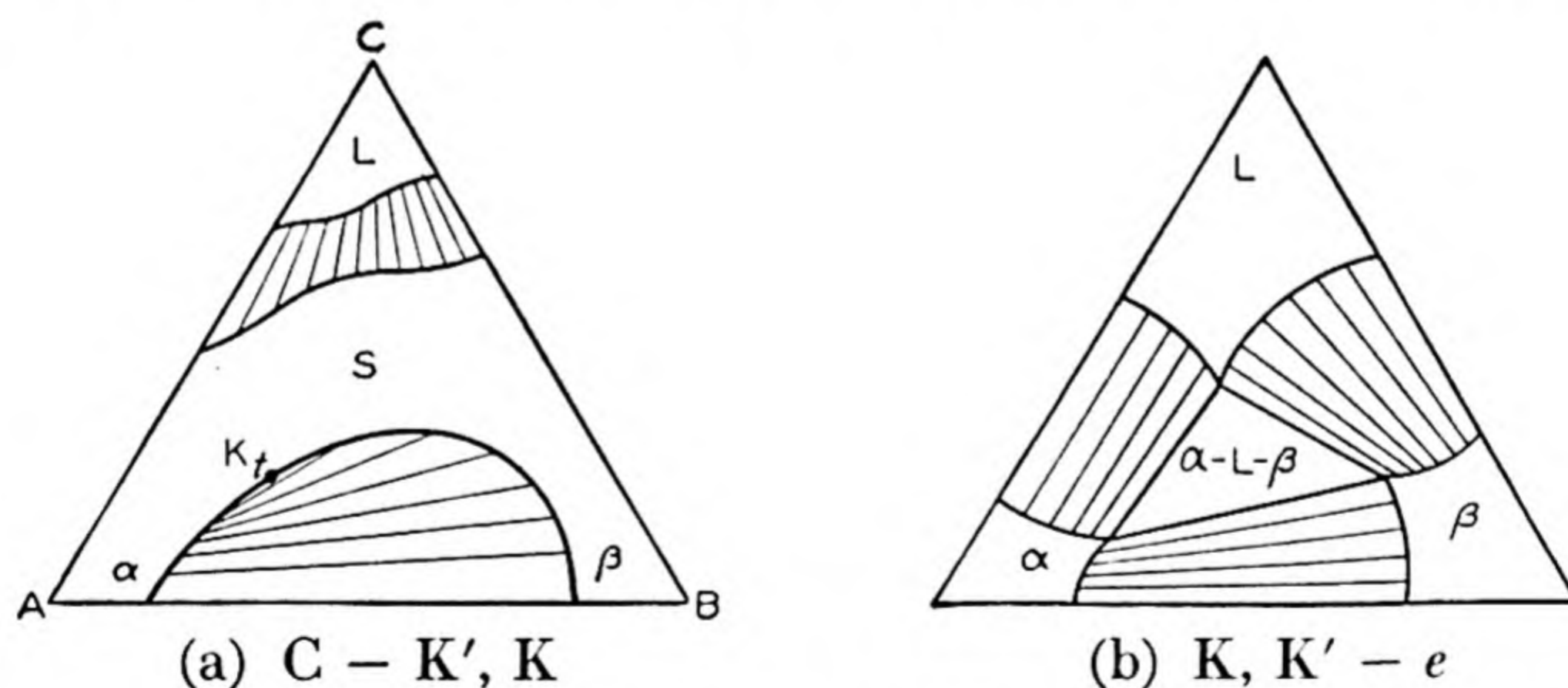


FIG. 11-56. Isotherms of Fig. 11-53 (b).

section, sK , the curve is approached from the A side and it is left on the B side. The dotted curve sy is the projection of the envelope of the $l\beta$ sides of even triangles approaching s with falling T ; the curve $K's'x$ is the projection of the envelope of the $l\alpha$ sides of 3-phase triangles approaching K from somewhere between z and s ; s' is merely that point of this projection involving the tie-line su , so that the envelope pertains to odd triangles between

s' and K and to even triangles between s' and x . For the symmetrical case, the eK curve never becomes odd, but there is still an envelope of tie-lines, and the points x and y are shown in the vertical section of Fig. 11-54.

Vertical sections, roughly normal to the line KK' , between K and the MG , appear as in Fig. 11-57, for the unsymmetrical case: (a) between K and s , (b) between s and the MG . The point m , now a minimum instead of a maximum as in 46(b), is at the same T in both sections, being on the line $K'K$. As the composition of the section is changed, away from the MG , m leaves the gap at K' , marking the change from a diagram of the type of 46(c) to 57(b). With further change in the position of the section the envelope of $l\alpha\beta$ tie-lines contracts, until it vanishes in the section through K itself.

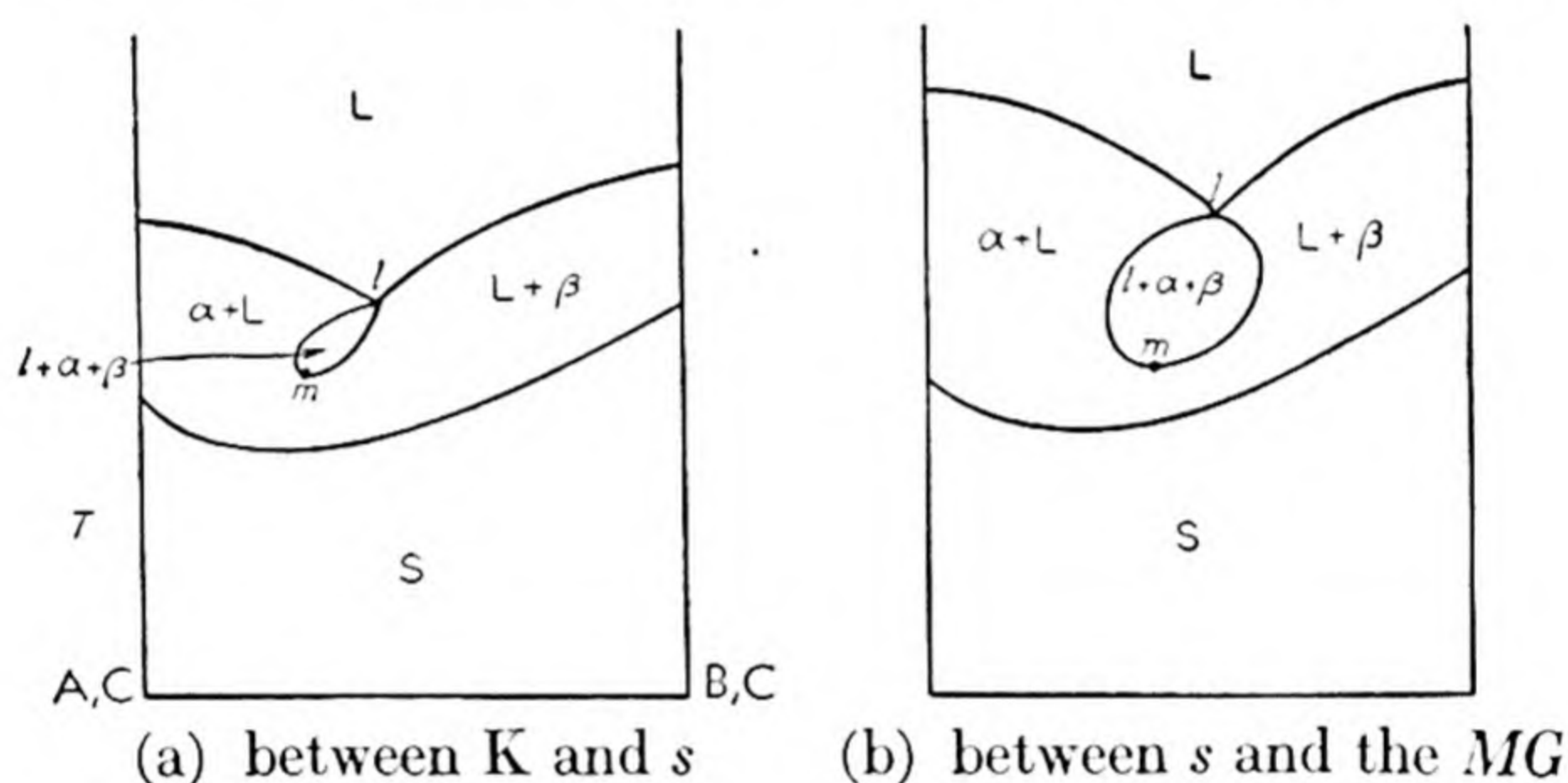


FIG. 11-57. Vertical sections of Fig. 11-53(b).

Between s and K (Fig. 11-57(a)), the $l\beta$ side of the envelope (curve lm on the B side) lies entirely to the left of l , in accordance with the “odd” nature of the curve in this region.

All liquids with compositions outside the boundaries (including the envelopes) of Fig. 11-53(b) solidify without any 2-solid equilibrium. Those in the MG , or in $aK'b$, must end as a mixture of $\alpha + \beta$, the last trace of liquid to solidify lying on the curve eK ; again the point K can be reached only if the original composition is on the line KK' . Those in the region $xs'Ksy$ solidify to a single solid, so that the final liquid does not lie on the curve eK , but they first pass through the equilibrium $l\alpha\beta$. Those on the a side of eK give “ α ,” those on the b side give “ β ,” as primary crystallization product, although such distinction between the solids has significance only on or in the MG . During the primary crystallization the liquid and solid change in composition until the liquid is on eK and the solid on $aK'b$, when the second solid begins to form. While the liquid is in twofold saturation, its composition moves toward K , and the solids begin to converge toward K' . For those on the y side of KK' , α is consumed during this process, whether or not it was the primary product; according to Fig. 11-57 this

means that the system passes out of the $l\alpha\beta$ envelope through the β side of the lm curve, leaving $l + \beta$. When all α is consumed, the liquid leaves the curve eK on the b side. For those on the x side of KK' , β is consumed, leaving $l + \alpha$; the system passes, on cooling, out of the envelope on the α side of m (Fig. 57), and then the liquid leaves the curve eK on the a side.

The sequence of solid phases for liquids with original compositions in the region zsy is therefore β , $\beta + \alpha$, β ; for those in $K'Kz$ it is α , $\alpha + \beta$, β ; and for those in xKK' it is α , $\alpha + \beta$, α . Liquids originating in svy , moreover, leave the curve along its even section sz , when α is consumed, to enter upon the β field, while those in xus' similarly leave the curve on this even section to travel on its left side, the α field, when β is consumed. All the others leave the curve for either side on the odd section sK . These relations are similar to those already discussed under Fig. 11-20.

Finally, as pointed out under Fig. 11-10, there may be either a maximum or a minimum of temperature on the curve $aK'b$, between K' and the binary side ab , at a colinear equilibrium for the three phases α , l , and β . The boiling point diagram of the system benzene (A)–water (B)–alcohol (C) exhibits such a minimum-boiling 2-liquid system, already mentioned in section B-1 of this chapter. The boiling point diagram at atmospheric P is shown, in schematic relations, in Fig. 11-58, in which the arrows indicate the direction of rising temperature during the process of boiling. There are two binary minimum-boiling azeotropes, m_1 and m_2 , and the 2-liquid equilibrium aeb is the minimum boiling point of the binary system benzene–water. The minimum boiling point of the ternary system, however, is the line xmy , which is to be compared with that in Fig. 11-10(b).

These relations form the basis of the dehydration of alcohol by benzene distillation first proposed by Young.⁵ If aqueous alcohol with composition near m_1 is mixed with benzene to give a ternary composition such as P above the line xmy , the system begins to boil as a 2-liquid system $\alpha_1 + \beta_1$, giving off the vapor v_1 . As the boiling proceeds the temperature rises gradually and the liquid compositions travel toward K' while the vapor moves toward K . The relations of the system above the line xmy are, in other words, like those of Fig. 11-52(b). During the boiling the β liquid phase is being consumed, and it disappears entirely when the point P is swept by the tie-line α_2v_2 . [With removal of vapor the residual composition does not remain fixed at the original point P but moves toward the curve α_1K' in a direction away from the composition (itself changing along the curve v_1K) of the vapor which is being distilled; it is only for simplicity of representation that it has been assumed to remain fixed at P in the schematic diagram of Fig. 11-58.]

⁵ S. Young, *J. Chem. Soc.*, **81**, 707, 739 (1902).

At this point the residual liquid leaves curve xK' to rise in boiling point toward the maximum C. The distillate collected to this point, or the first fraction, has a composition on the vapor curve between v_1 and v_2 . The quantitative relations are such that practically all of the water will have been removed in the form of this vapor constituting the first fraction, since

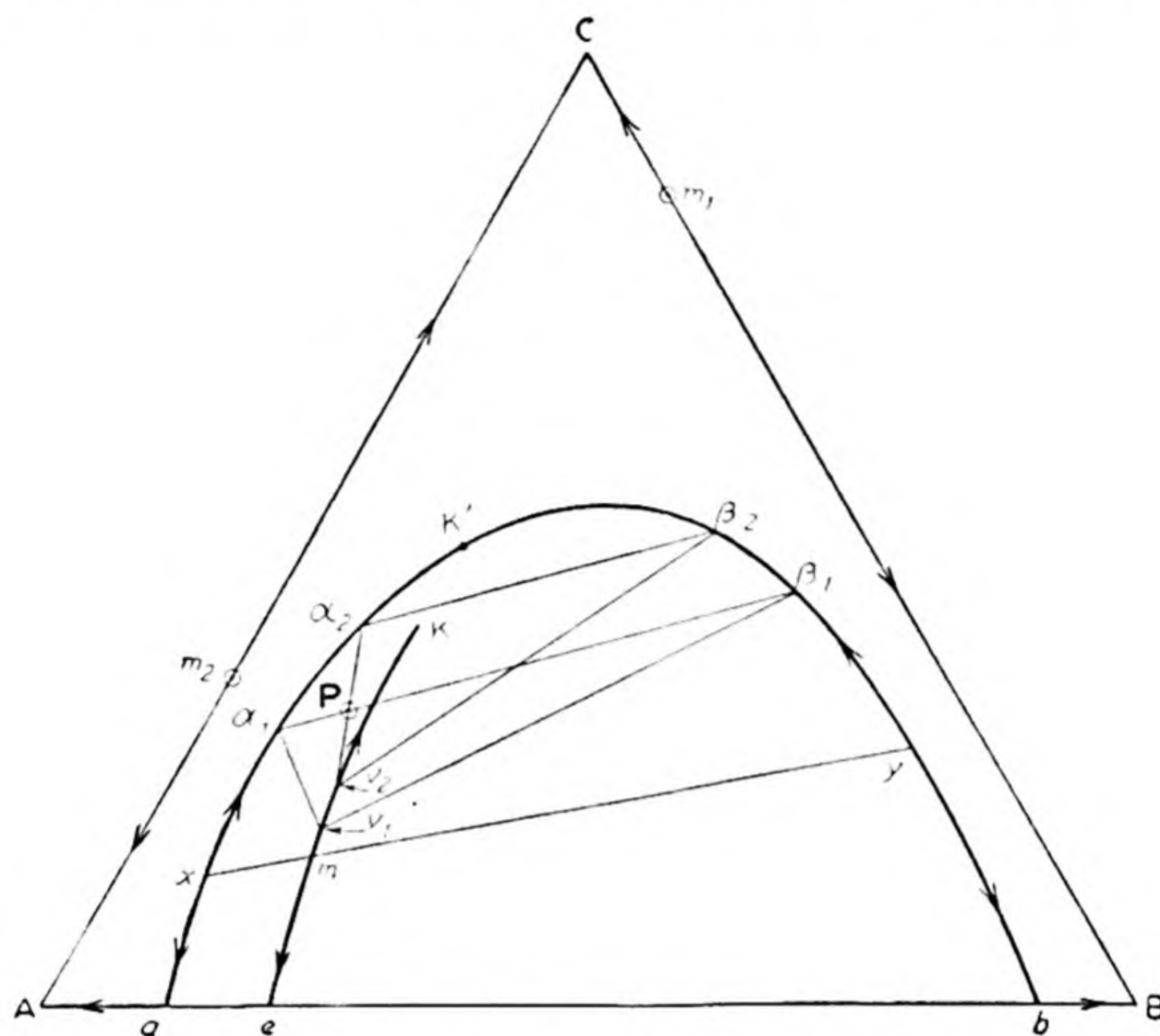


FIG. 11-58. Boiling point diagram (schematic) for system benzene (A)-water (B)-alcohol (C).

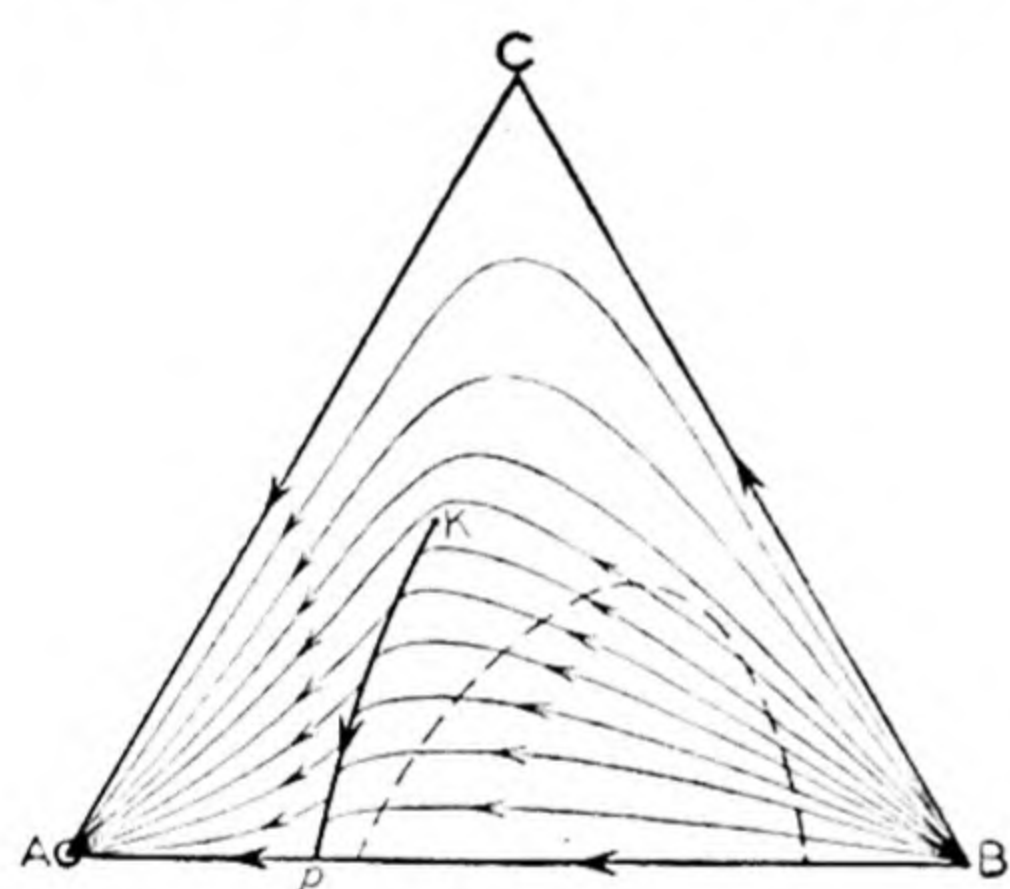
α_2 lies very close to the AC side of the triangle. The subsequent distillation is therefore essentially the ordinary distillation of what is effectively the binary system A-C, starting on the C side of the minimum-boiling azeotrope m_2 . The second fraction is therefore a vapor with composition approximating m_2 , and the residual liquid, or the third fraction, approaches pure alcohol, C, in composition. The first fraction, or the vapor v_1v_2 , moreover, condenses on cooling into two liquid layers, a "benzene layer" with composition on the curve aK' for the system at the temperature of the condensation, and what may be called an "aqueous layer" on the curve bK' . The first layer is used again for the benzene distillation process and the second is treated separately for the recovery of both alcohol and benzene. In the present day continuous process,⁶ the aqueous alcohol (94%) is treated with benzene in a fractionating column; the vapor, with composition on the curve mK , is drawn off from the head of the column, and anhydrous alcohol from the base. The benzene layer from the condensation of the

⁶ For a review and data, see W. S. Norman, *Trans. Institution of Chemical Engineers*, **23**, 66 (1915).

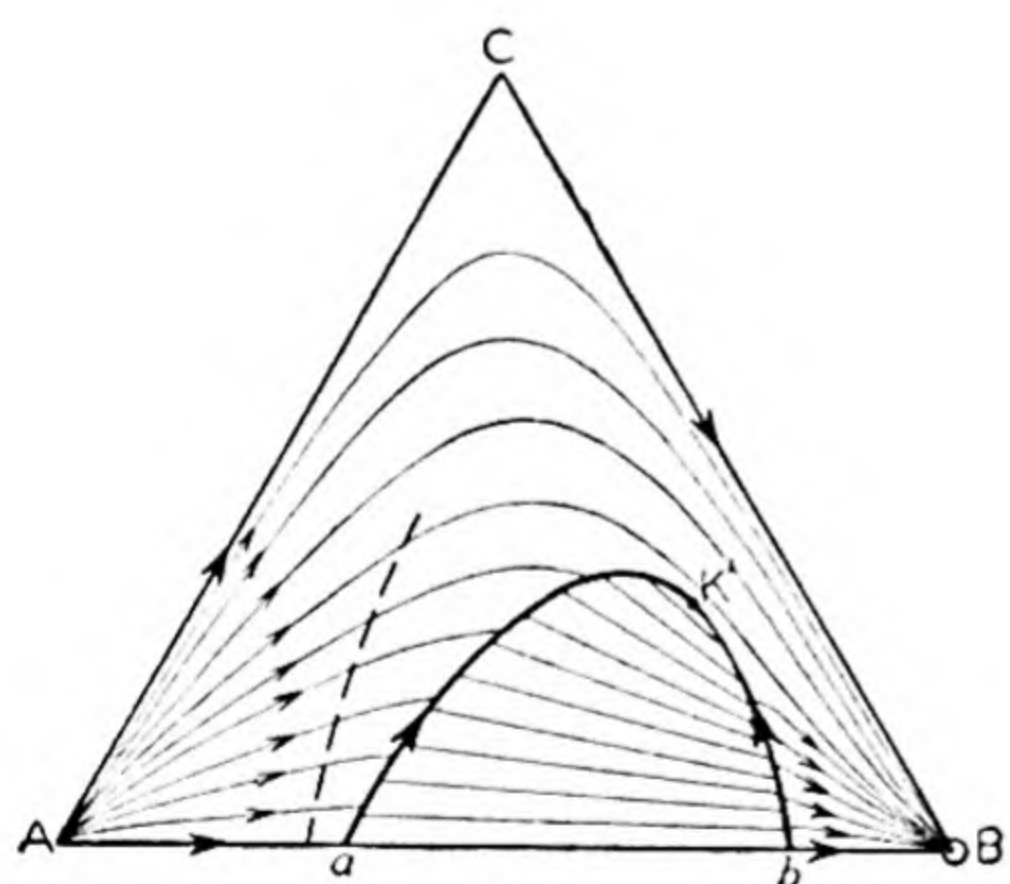
is now $pKxK'b$, in which Kx is the projection of the envelope of $l\alpha$ tie-lines ($l\alpha$ sides of the $l\alpha\beta$ triangles) not enclosed by $pKK'b$; Kx is not a tangent from K to the MG but a curve, convex to the pab base line. For all liquids in the region $pKK'b$ the solidification process may be said to be normal, with β as primary solid, the liquid and solid then changing in composition until l reaches pK and β reaches bK' , when α appears on curve aK' . Then the liquid moves along pK toward p , while α and β move on the $aK'b$ curve away from K' . If the composition is in the MG , liquid disappears before reaching p , leaving $\alpha + \beta$. Otherwise β disappears, leaving $l + \alpha$, whereupon the liquid crosses the odd-reaction curve to the A side, finally solidifying to α completely.

Liquids in the region KxK' must be said to form α as the first phase and β as the second when the liquid reaches curve pK and the solid reaches the curve xK' . For those with original composition, P , in the MG , P comes to be swept, with falling T , by the $\alpha\beta$ tie-line, when all the liquid is consumed,

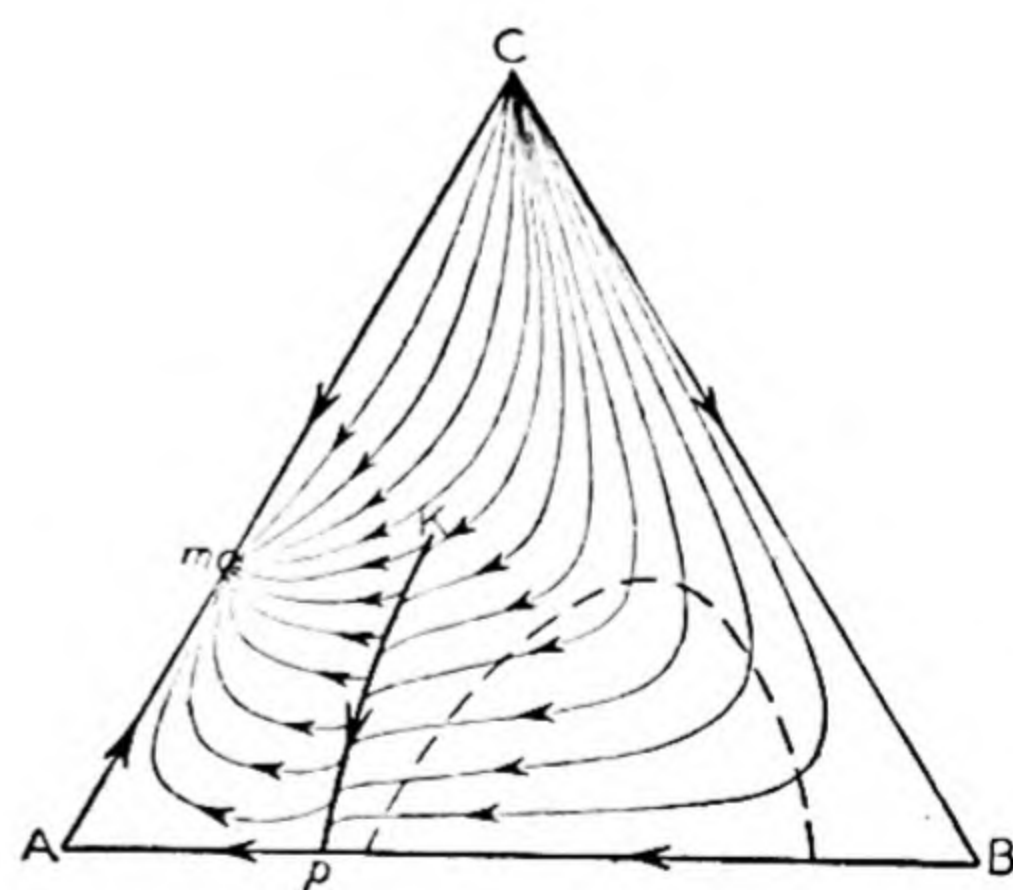
leaving $\alpha + \beta$. For those outside the MG , P comes to be swept again by the $l\alpha$ tie-line, when β disappears again to leave $l + \alpha$. Then the liquid crosses the curve pK , to solidify completely to α of composition P . The sequence of solid phases for compositions in the envelope region Kxz is therefore α , $\alpha + \beta$, α .



(a)



(b)



(c)

FIG. 11-60. Transition surfaces of Fig. 11-59.

Fig. 11-60(a) shows the crystallization paths for effective removal of solid during solidification, assuming $B > C > A$; 11-60(b) shows boiling point paths for the same case; and 11-60(c) represents the crystallization paths

for a variation, such as $C > B$ and a minimum in the A–C binary system. In 11-60(b) it may be seen that ternary liquids with compositions such that the boiling point paths lead to the curve aK' will pass temporarily through a 2-liquid state during distillation, the liquid residue always approaching pure B. Moreover, if the directions of the arrows in 11-60(b) are reversed, we have the isothermal vapor pressure diagram of a ternary liquid system with limited miscibility only in the A–B system. The composition of the vapor produced upon isothermal evaporation of the 2-liquid system falls on the curve pK . Such a diagram is given by the system water (A)–phenol (B)–acetone (C) at 56.5° ,⁸ with the possible variation that there is apparently a slight pressure maximum in the binary system A–B between A and a .

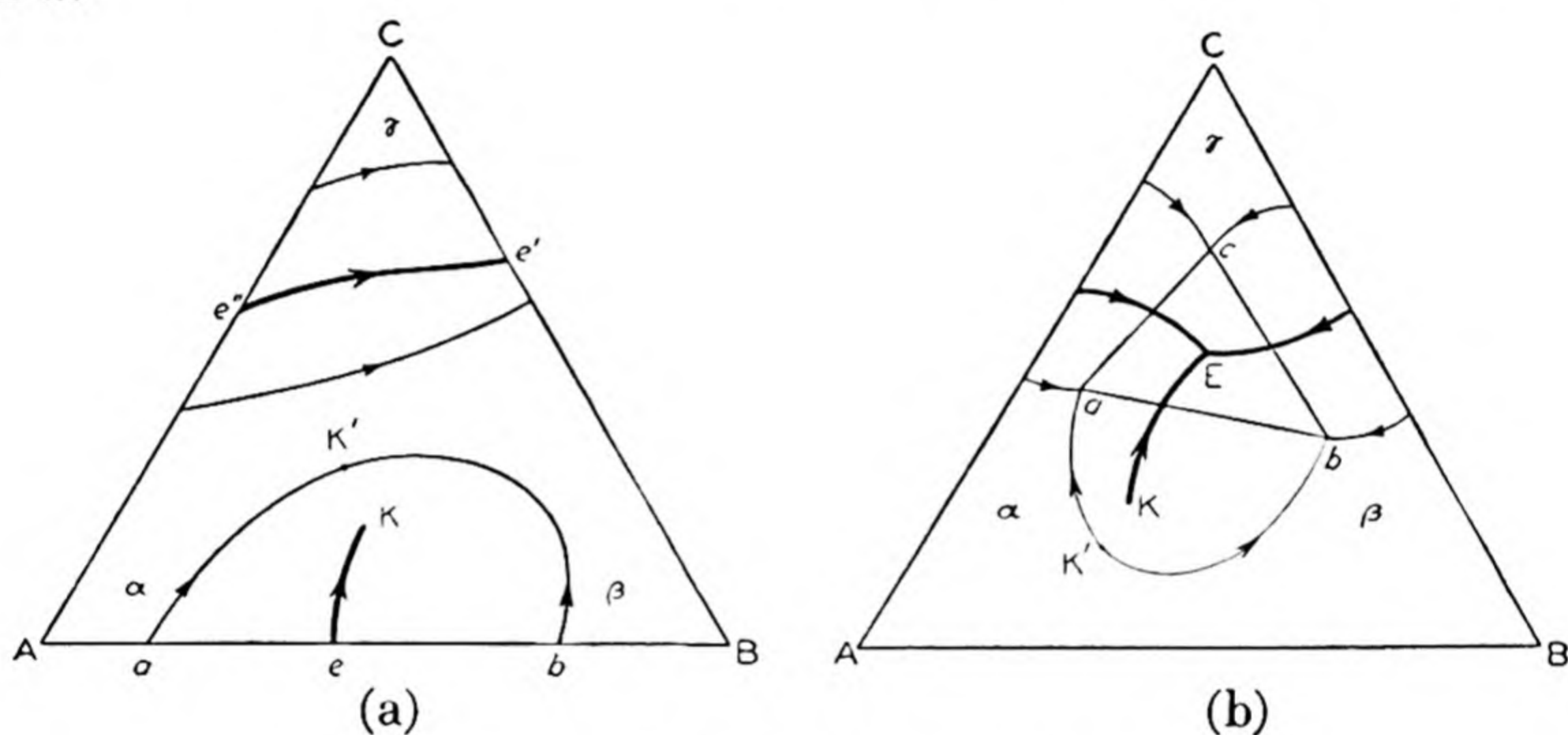


FIG. 11-61. More than one *MG*.

The case discussed in the present section (that is, section D) may be only one element of a complete ternary system. The systems A–C and B–C may themselves have solid immiscibility at the melting point curves, so that between the sides AC and BC there may occur a continuous curve of 3-phase equilibrium, as in Section B of this chapter, but not reached by the 3-phase equilibrium originating at the system A–B, which ends as here described, at a critical solution point (Fig. 11-61(a)). On the other hand, the ternary system may be of the eutectic type of section C-1, and one or more of the eutectic curves may fail to reach the side of the prism with increasing T . This occurs if the binary system A–B, for example, gives a continuous melting point curve (Fig. 11-61(b)). In this case the eutectic curve EK is to be imagined as starting at the ternary eutectic, as a 3-phase triangle $\alpha E\beta$, and rising in T in the direction of the AB side, to end at a critical solution point of the type of K, K' of Fig. 11-49.

⁸ F. A. H. Schreinemakers, *Z. phys. Chem.*, **40**, 440 (1902).

Chapter XII Transitions Involving Pure Solid Phases

A. Solid Solution in One Binary System (A-C)

The component B is assumed immiscible with A and C in the solid state, while A and C form binary solid solution (S). Now the systems A-B and B-C must be eutectic. (The case in which a binary compound in the system A-B forms solid solution with a corresponding compound in the system A-C is discussed in section D of this chapter.)

1. The AC Solid Solution Is Continuous

Fig. 12-1 shows the case involving no maximum or minimum of the AC melting point curve. The liquidus is divided into two parts: Bee' (e and e' being the binary eutectics) for the primary crystallization of pure B, and

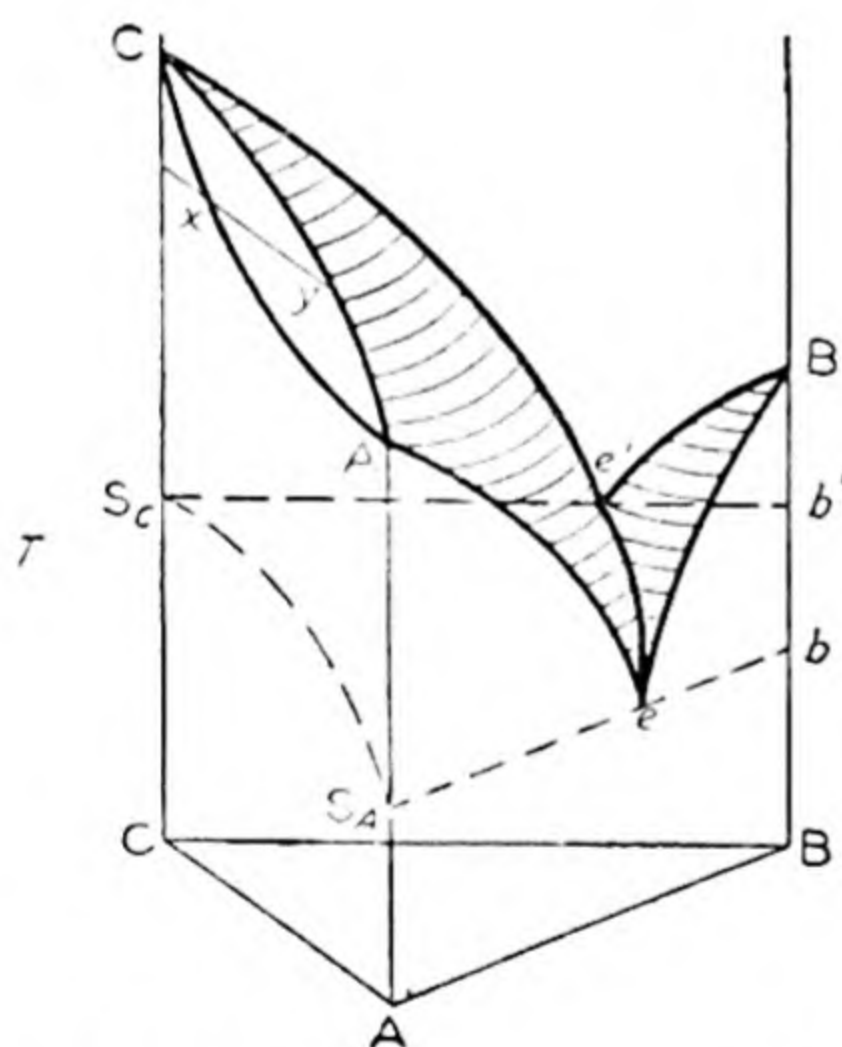


FIG. 12-1. Solid solution only in AC (continuous).

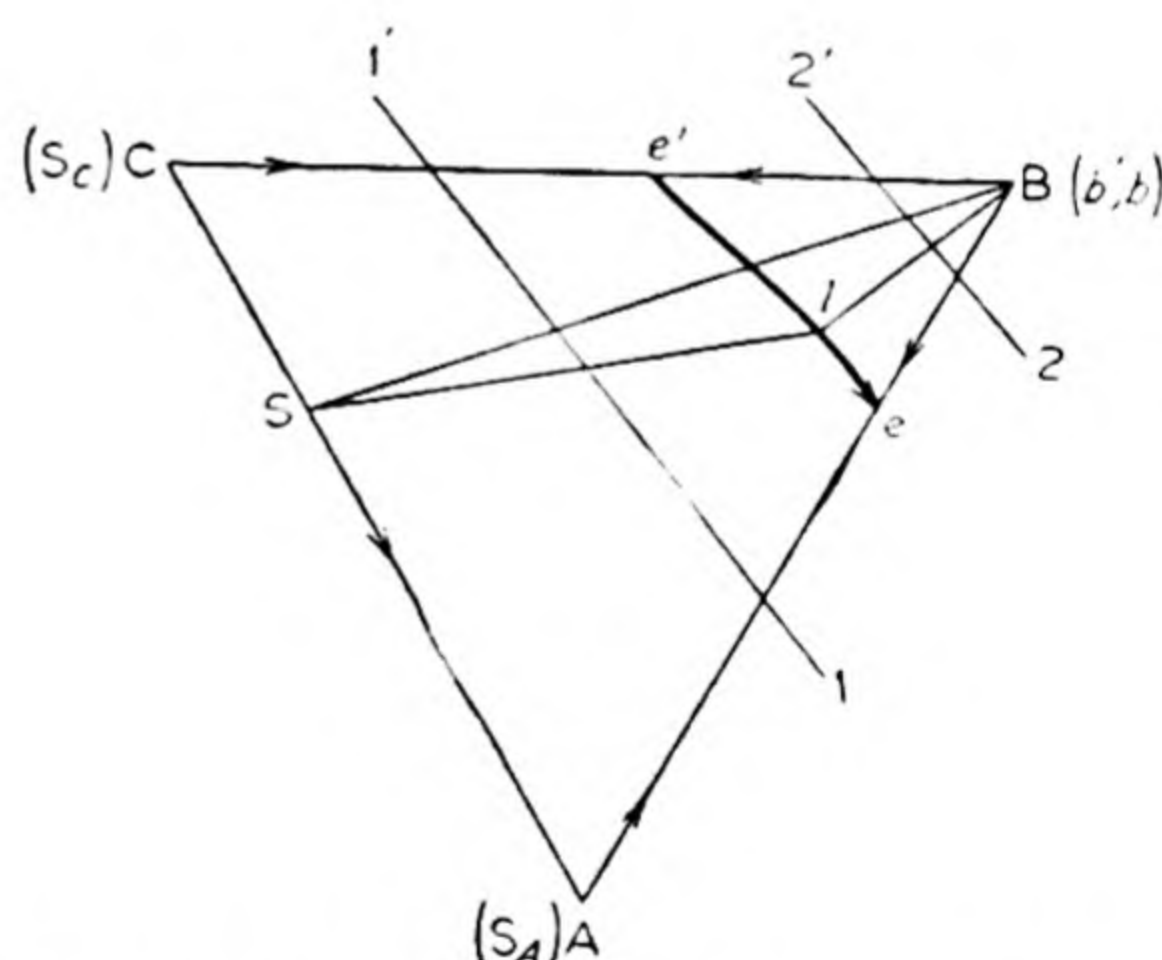


FIG. 12-2. Polythermal projection of Fig. 12-1.

$CAee'$ for primary crystallization of AC binary solid solution, to be called S. If $e' > e$, the 3-phase line $Sce'b'$ ($b' = \text{pure B}$, $S_C = \text{pure C}$) moves across the prism as the 3-phase triangle S/B to S_Aeb (Fig. 12-2). The vertical sections 1'-1, 2'-2, and S-B of Fig. 12-2 are shown in Fig. 12-3. The boundaries of the region $L + S + B$ in Fig. 12-3 are not solubility surfaces, but, as in Fig. 11-7, they are points on tie-lines, the upper curve cutting the tie-lines Sl , the lower the tie-lines SB , in Fig. 12-3(a).

With $A > B$, some isotherms are given in Fig. 12-4. The tie-lines in Fig. 12-4(a) for liquid in equilibrium with a binary solid solution running from pure C to point x (Fig. 12-1), connect, without crossing, the liquid curve zy with the straight line Cx . The limiting tie-line on each side is

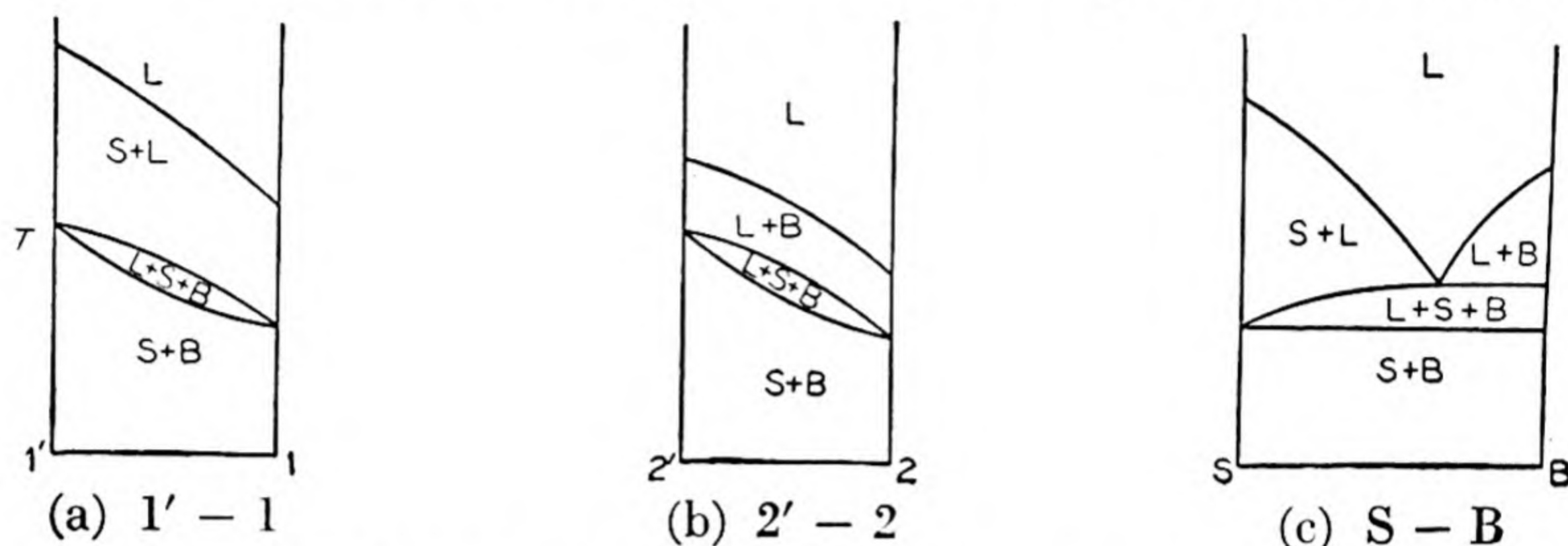


FIG. 12-3. Vertical sections of Figs. 12-1 and 12-2.

binary, lying on the side of the triangle. In Fig. 12-4(b), below the melting point of A, the tie-lines run from C to pure A. This is typical for the isotherm of water and two isomorphous salts with common ion, forming continuous solid solution. In Fig. 12-4(c), below the melting point of B (for

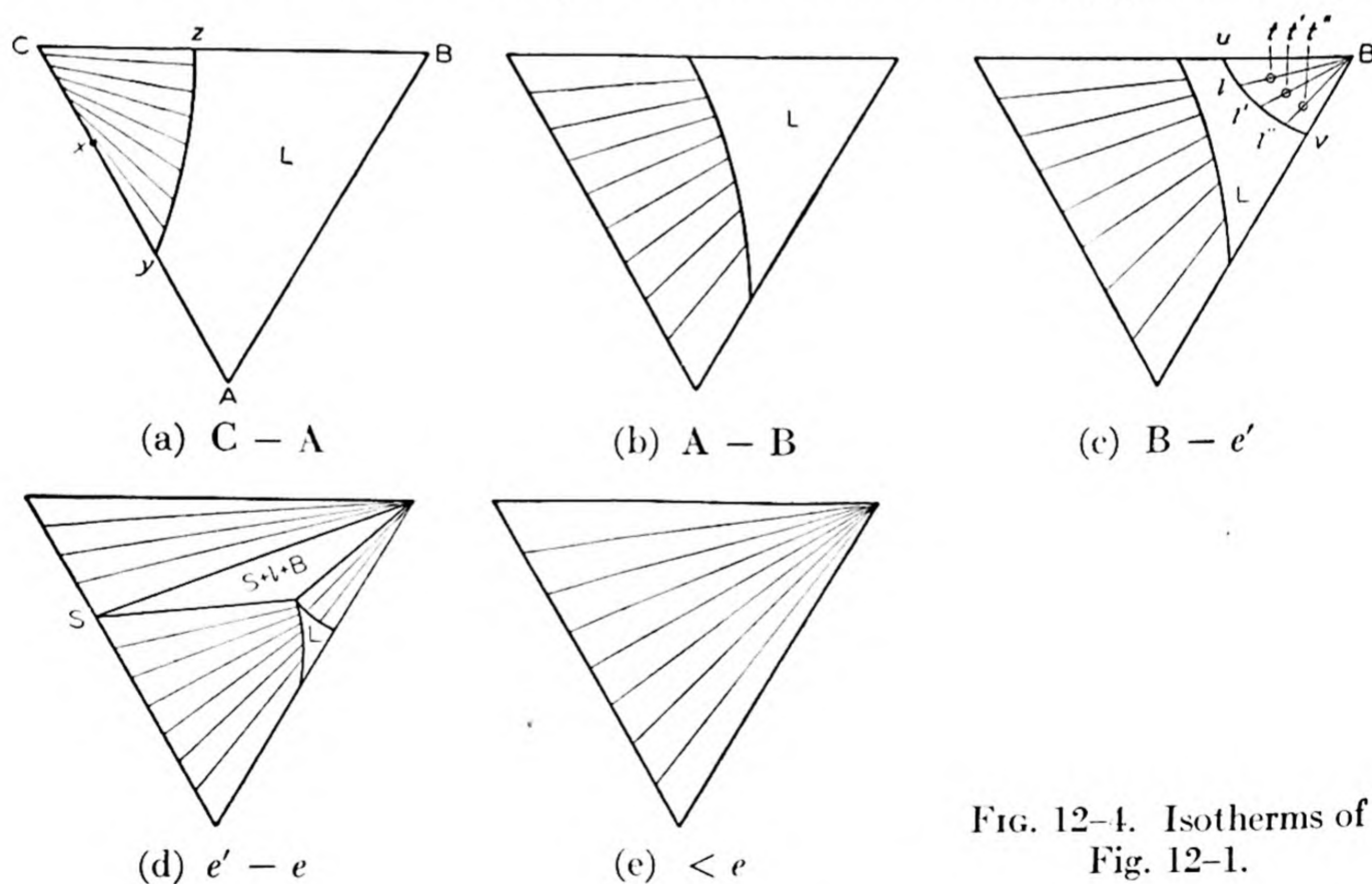


FIG. 12-4. Isotherms of Fig. 12-1.

example, ice), the curve uv is the solubility curve of pure B in the ternary liquid, at the T of the isotherm. The tie-lines run to the corner. In 12-4(d), below the eutectic e' , the triangle lSB is that shown in Fig. 12-2. Solid solutions between C and point S are in equilibrium with pure solid B; those

between S and A are saturating the liquid phase. Tie-lines are also drawn between CS and B, as a mixture of two solid phases, since compositions in this region, made up of A, C, and B, form, at equilibrium, two phases, pure B and a binary solid solution of A + C. Hence Fig. 12-4(e), below e , shows such a field occupying the whole diagram.

The tie-lines in the isotherm 12-4(b) may or may not include one in which the ratio A/C is the same both in the liquid and in the solid phase, that is, a line directed through the corner B. The significance of the disposition of the tie-lines, with respect to the corner B (the solvent), will be discussed in Chapter XIII (Fig. 13-25).

A liquid with composition in region Bee' of Fig. 12-2 precipitates pure B when cooled to the B surface of Fig. 12-1. During precipitation of B, the composition of the liquid moves on this surface toward the curve ee' in such a way that the projection of its course on the composition plane is a straight line through pure B. This is not the case for a liquid on the surface $Ce'eA$, precipitating the solid solution S as primary solid; in

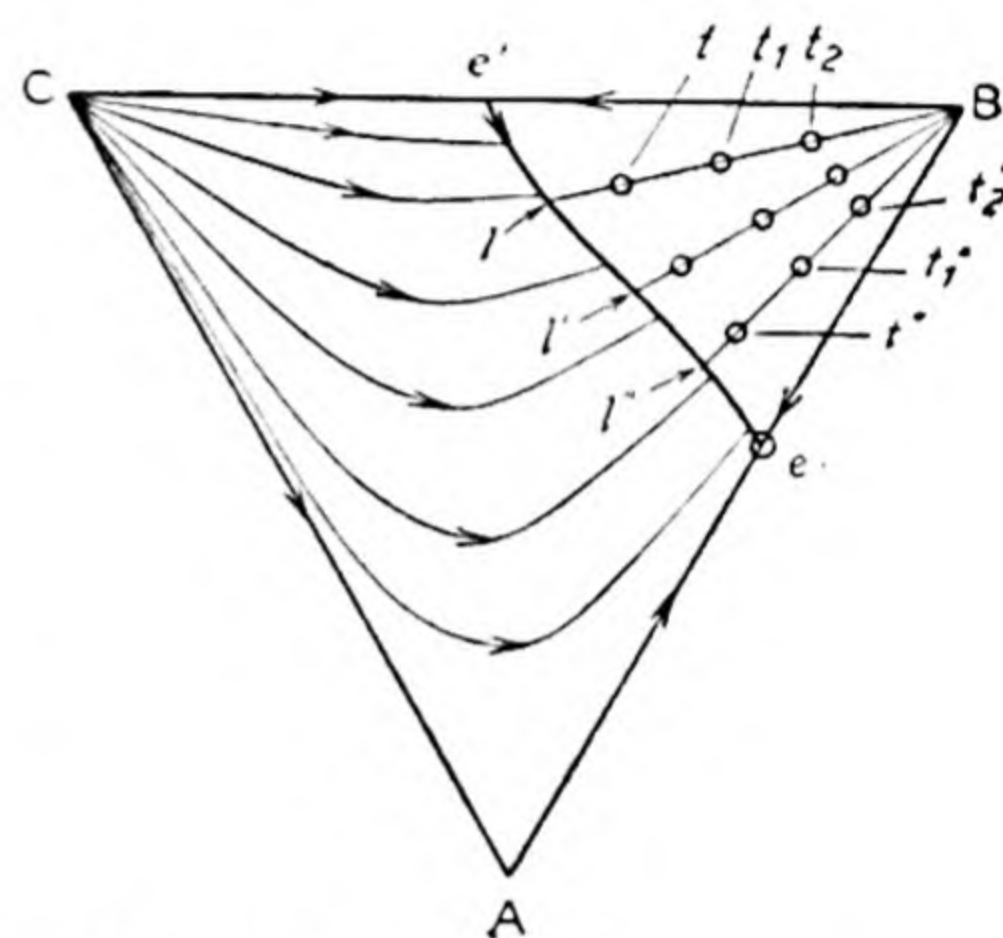


FIG. 12-5. Crystallization paths for Fig. 12-1.

this case the projection of the course of the liquid, toward ee' , is a curve determined by the effect of T on the direction of the tie-lines in the solid-liquid equilibrium of the system. The crystallization paths are shown projected in Fig. 12-5; while all the paths in $Ce'eA$ are curved, those in the B field are straight lines converging at B.

A pure solid phase may therefore be distinguished in two ways from a solid solution, in the ternary equilibrium of liquid + solid. The isothermal tie-lines (Fig. 12-4) converge to a single point on the isothermal diagram, if the saturating solid is a pure solid, whereas those for a solid solution end upon a line (or curve) representing the range of composition of the saturating solid. In Fig. 12-4(c) the point t is the composition of a mixture of solid B and its saturated ternary solution l . The line drawn through l and t , and extended away from l , must be a tie-line of the 2-phase region. If such tie-lines then converge to a point on the diagram, the saturating phase is a pure solid. In this way we may not only distinguish a pure solid from a solid solution, but also, for a pure solid, determine its composition from the convergence of the tie-lines. Similarly, the crystallization paths, during cooling, are curved for the separation of a solid solution and straight lines converging to a point for the crystallization of a pure solid. This means that, although the liquids t , t_1 , t_2 , of Fig. 12-5 give different temperatures of primary

crystallization, they all give a break at the same temperature to mark the start of secondary crystallization, since they all reach the curve ee' at the same point l . If, therefore, we plot the compositions of liquids giving the same primary phase and the same secondary temperature break in thermal analysis, we have a series of lines converging at the composition of the primary solid phase. These are two methods, one using isothermal solubility determinations, the other thermal analysis, for the determination of the composition of a solid in a ternary system without isolation and analysis.

A crystallization path may also be plotted by using a single sample and analyzing the saturated liquid at various temperatures. The successive liquid compositions describe a crystallization path which will be a straight line in the field of saturation with a pure solid. The various straight line crystallization paths in any field, moreover, diverge, with falling T , from the composition of the solid. If the paths are plotted, therefore, and extended back to an intersection, they may be used for fixing the composition of the solid.¹

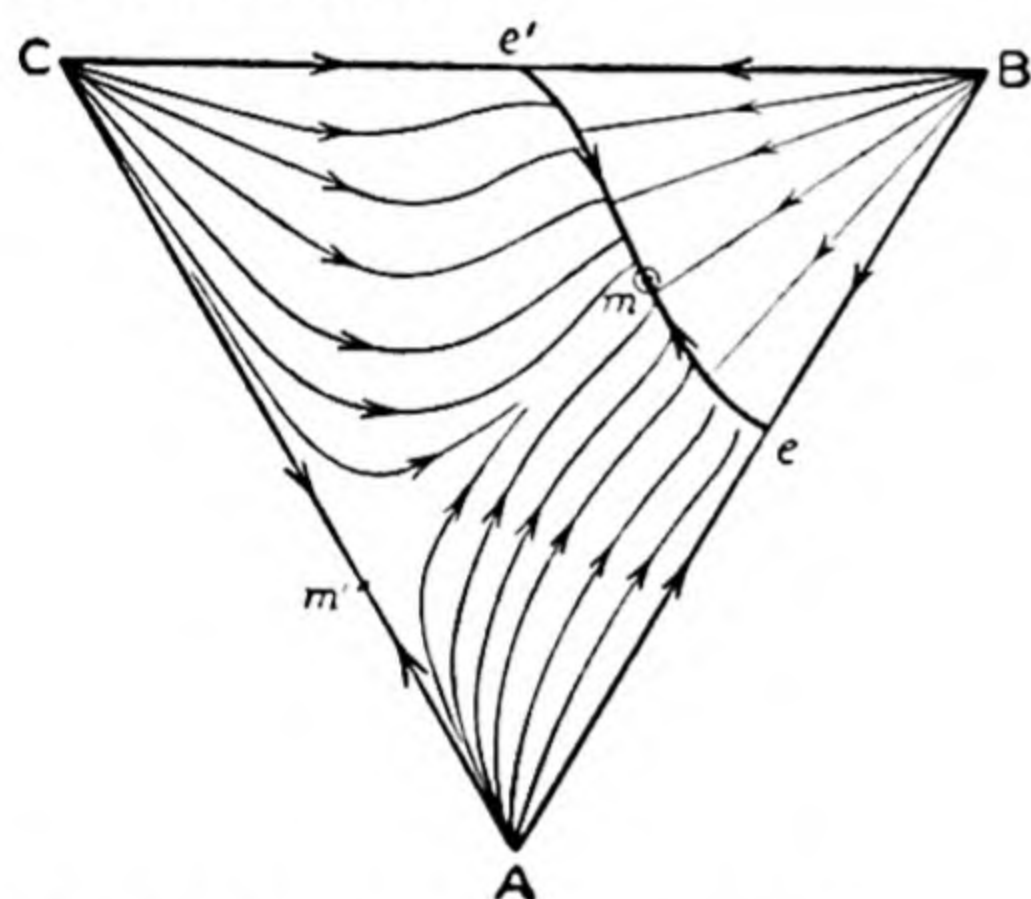


FIG. 12-6. "Azeotropic" variation of Fig. 12-5.

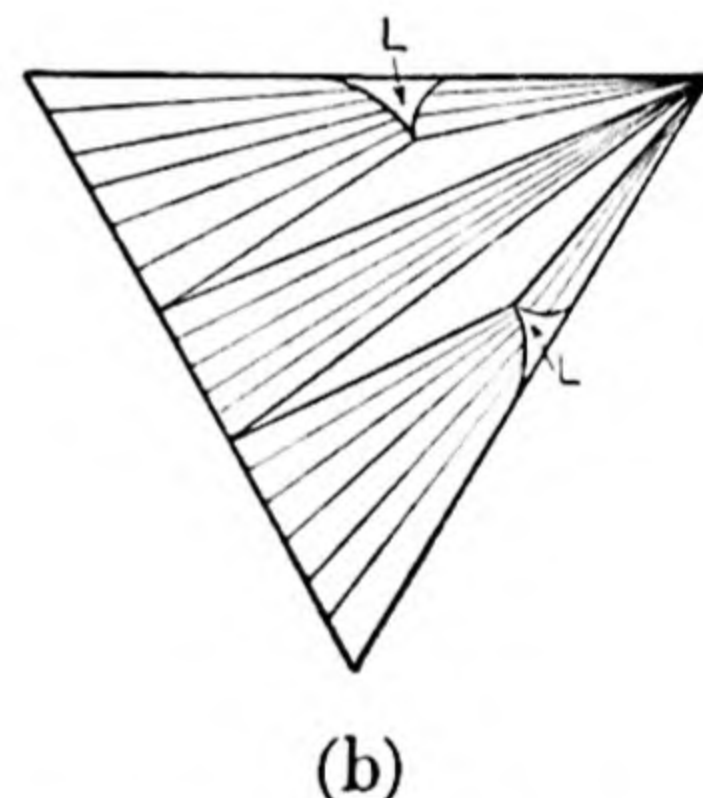
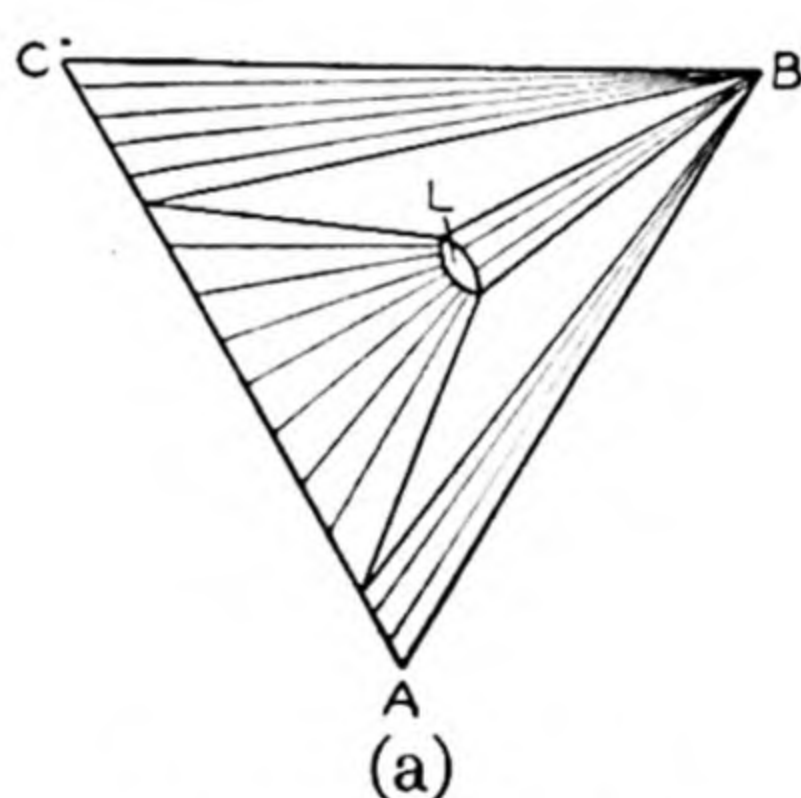


FIG. 12-7. Isotherms for minimum (a) or maximum (b) in curve ee' .

The system of Figs. 12-1 to 12-5 is illustrated by PbBr_2 (A)– PbI_2 (B)– PbCl_2 (C)² and by $\text{NaAlSi}_3\text{O}_8$, albite (A)– $\text{CaMg}(\text{SiO}_3)_2$, diopside (B)– $\text{CaAl}_2\text{Si}_2\text{O}_8$, anorthite (C).³

The eutectic curve ee' may also have a minimum or a maximum, usually accompanying an "azeotropic" type of curve for the binary system A–C. The ternary minimum (Fig. 12-6) would be a crystallization end-point for freezing with effective removal of solid. Figs. 12-7(a) and 12-7(b) are isotherms just above a minimum and just below a maximum, respectively;

¹ As explained and demonstrated by T. R. Briggs in the study of the solid polyiodides (hydrated and anhydrous) of the alkali group; cf. T. R. Briggs, K. H. Ballard, F. R. Alrich and J. P. Wikswo, *Jour. Phys. Chem.*, **44**, 325 (1940), and T. R. Briggs, K. D. G. Clack, K. H. Ballard and W. A. Sassaman, *ibid.*, **44**, 350 (1940).

² *I. C. T.*, IV-50, 51, 80.

³ N. L. Bowen, *Z. anorg. Chem.*, **94**, 23 (1916).

the minimum or maximum would be a colinear equilibrium similar to that mentioned under Fig. 11-10. Fig. 12-8(a) is an isotherm just above a binary minimum in A-C, the minimum being assumed to be higher than the melting point of B; and Fig. 12-8(b) is an isotherm just below a binary maximum in A-C. The solution c , in either figure, is saturated with solid solution x , a with y , c' with pure C, and a' with pure A. An example of Fig. 12-6 is the system SrCl_2 (A)- NaCl (B)- BaCl_2 (C).⁴

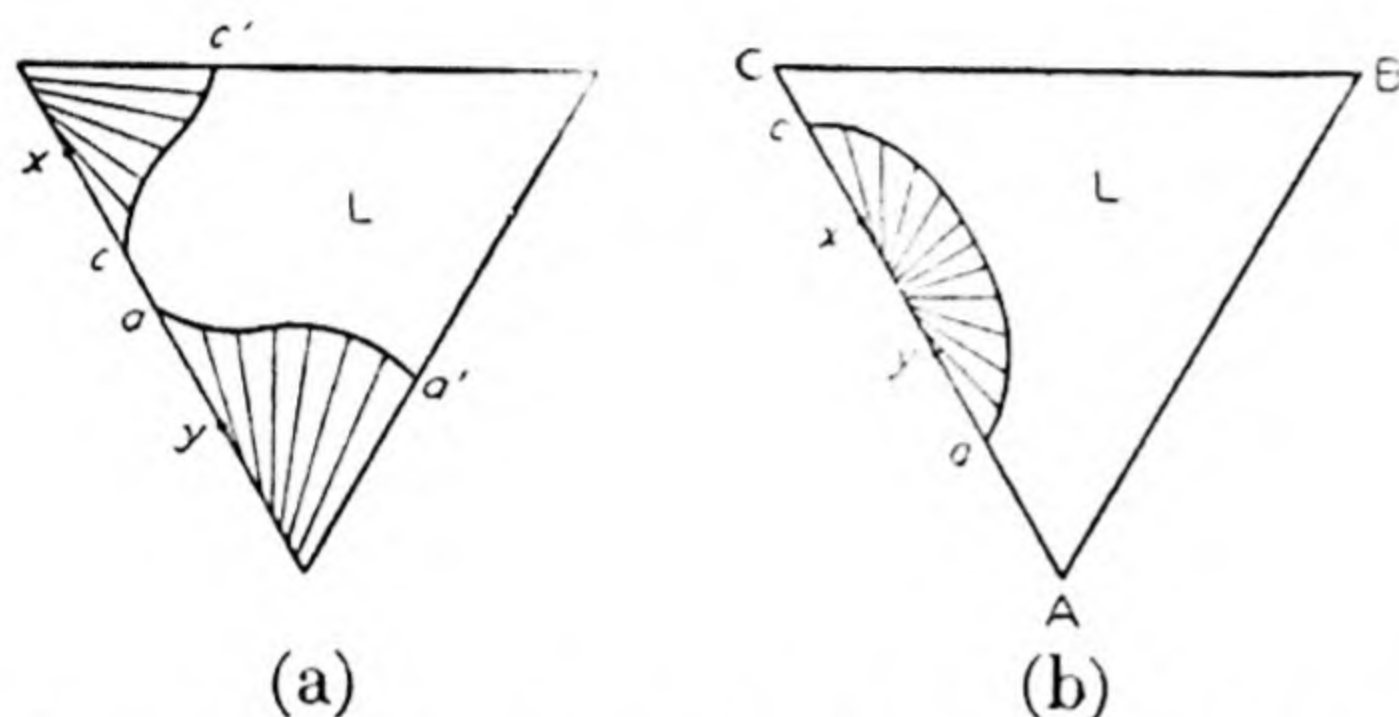


FIG. 12-8. Isotherms for minimum (a) or maximum (b) in system AC.

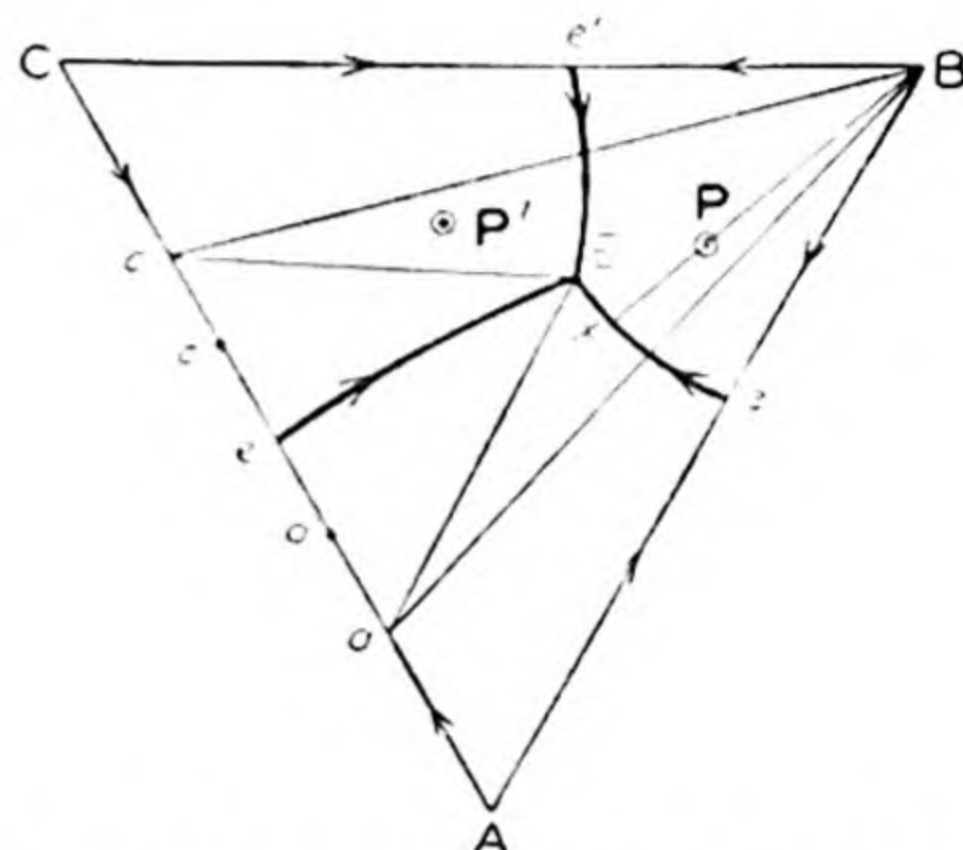


FIG. 12-9. MG in system AC, with a eutectic.

2. The Binary Solid Solution (AC) Is Discontinuous, with a Eutectic e''

We shall call the A-rich solid solution α and the C-rich solid solution γ . Now there is a ternary eutectic E, shown on the projection (Fig. 12-9) as the invariant eutectic plane cBa , with the liquid E contained in it. The 3-phase triangles cBl and aBl have the same meaning as SBl of Fig. 12-2, one falling to the eutectic from each of the binary sides BC and AB. That from BC starts as the line $Ce'B$, and, as T falls, C becomes a binary solid solution (γ) containing A, reaching the point c at the eutectic T . The points c and a are therefore the ends of a tie-line of the MG of the system A-C, at the temperature of E. The 3-phase eutectic curve from side AC starts as the line $c'e''a'$; if the MG widens as T falls, then as the liquid approaches E on $e''E$, the solids move toward c and a respectively. If $e'' > B$, the representative isotherms are those of Fig. 12-10. Fig. 12-10(b) is typical for the system water (=B) and two isomorphous salts, with common ion, forming limited solid solution. Experimentally it is possible for one of the salts to be pure, all the tie-lines in its field converging at the corner, while the other solid phase has a variable composition.

Liquids in the regions CcB and AaB of Fig. 12-9 solidify before reaching E to a mixture of $B + \gamma$ (C-rich crystals lying on Cc) or $B + \alpha$ (A-rich crystals on Aa) respectively. Only those in the triangle cBa reach the eutectic to leave a 3-solid mixture.

⁴ I. C. T., IV-82.

If a liquid (P) in the B field (Fig. 12-9) is cooled, the straight-line crystallization path, through B and P , determines whether the secondary crystallization will be the C -rich binary crystals γ , or the A -rich crystals α , since the line BP determines which of the two eutectic curves, $e'E$ and eE , will be reached (at point x). If, furthermore, the temperature contours on these

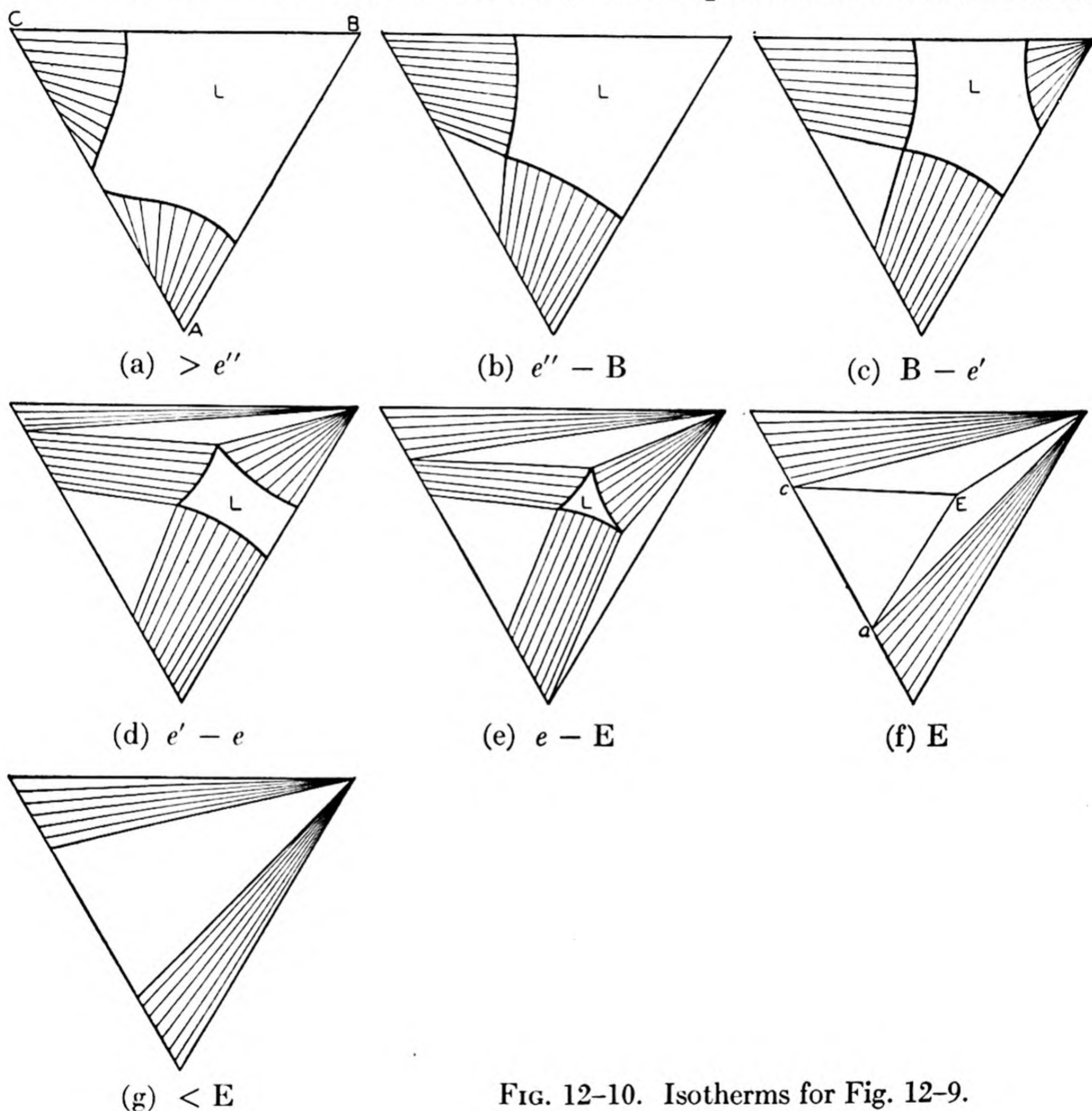


FIG. 12-10. Isotherms for Fig. 12-9.

curves are known, the temperature of x also can be estimated. The liquid P' in a solid solution field forms γ as primary product. Being also in the triangle cBE , the liquid will reach the curve $e'E$ to give B as secondary product and then finally the eutectic. Liquids in the triangle cEa reach $e''E$, giving a mixture of binary crystals ($\alpha + \gamma$), and finally precipitate pure B in addition, at the eutectic. But the exact point and temperature at which such curves are reached from a field of crystallization of solid solution

cannot be determined without detailed analysis of the effect of T on the tie-lines involved, because of the curved nature of the crystallization paths.

3. The Binary Solid Solution (AC) Is Peritectic (point p , Fig. 12-11)

Now the peritectic curve from p meets the eutectic curves from e and e' at an invariant point Q_B , at a temperature between e and e' . The points c and a mark the MG of system A-C at Q_B . The invariant quadrangle cBQ_Ba is approached from high T by the even-reaction triangle γ/B from e' , and by the odd triangle $\gamma\alpha/B$ from p . At Q_B the stable diagonal changes from cQ_B to aB , and the stable systems below Q_B are $\gamma\alpha/B$ and α/B , leading to the eutectic e . The isotherms, for $A > B$, are shown in Fig. 12-12; below e we would have Fig. 12-10(g).

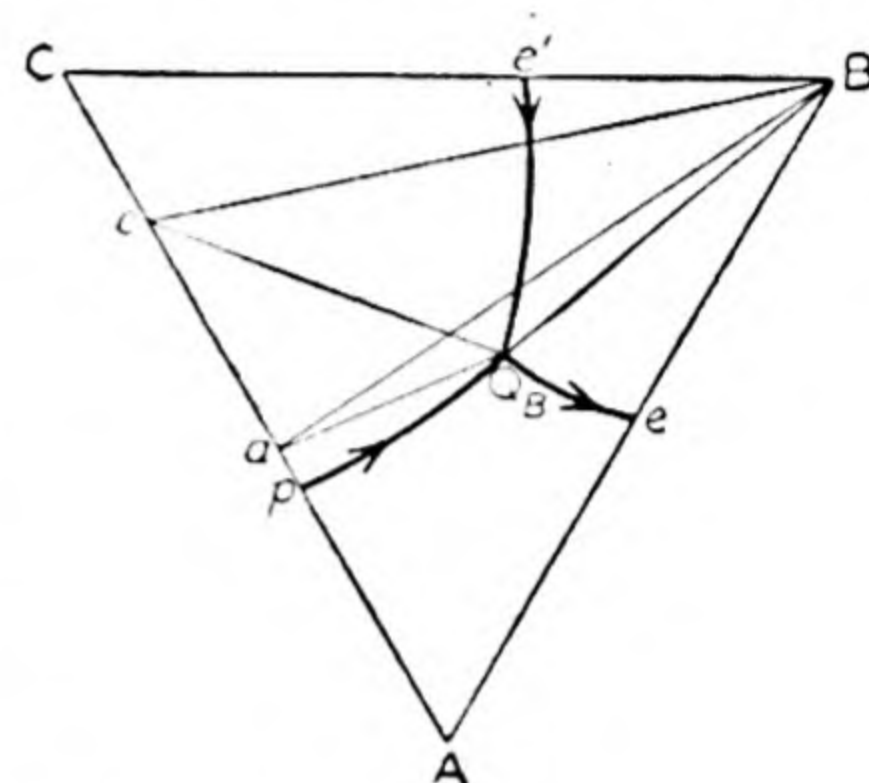


FIG. 12-11. MG in system AC, with a peritectic.

The primary crystallization product is determined by the position of a liquid with respect to crystallization surfaces: $CpQ_{Be'}$ for γ , ApQ_{Be} for α and $BeQ_{Be'}$ for B . The final state is determined with reference to the triangles CcB , cBa , aBA , leaving mixtures of $\gamma + B$, $a + B + c$ and $\alpha + B$, respectively. For liquids in the first of these triangles the secondary crystallization occurs on the curve $e'Q_B$, but the liquid solidifies completely before

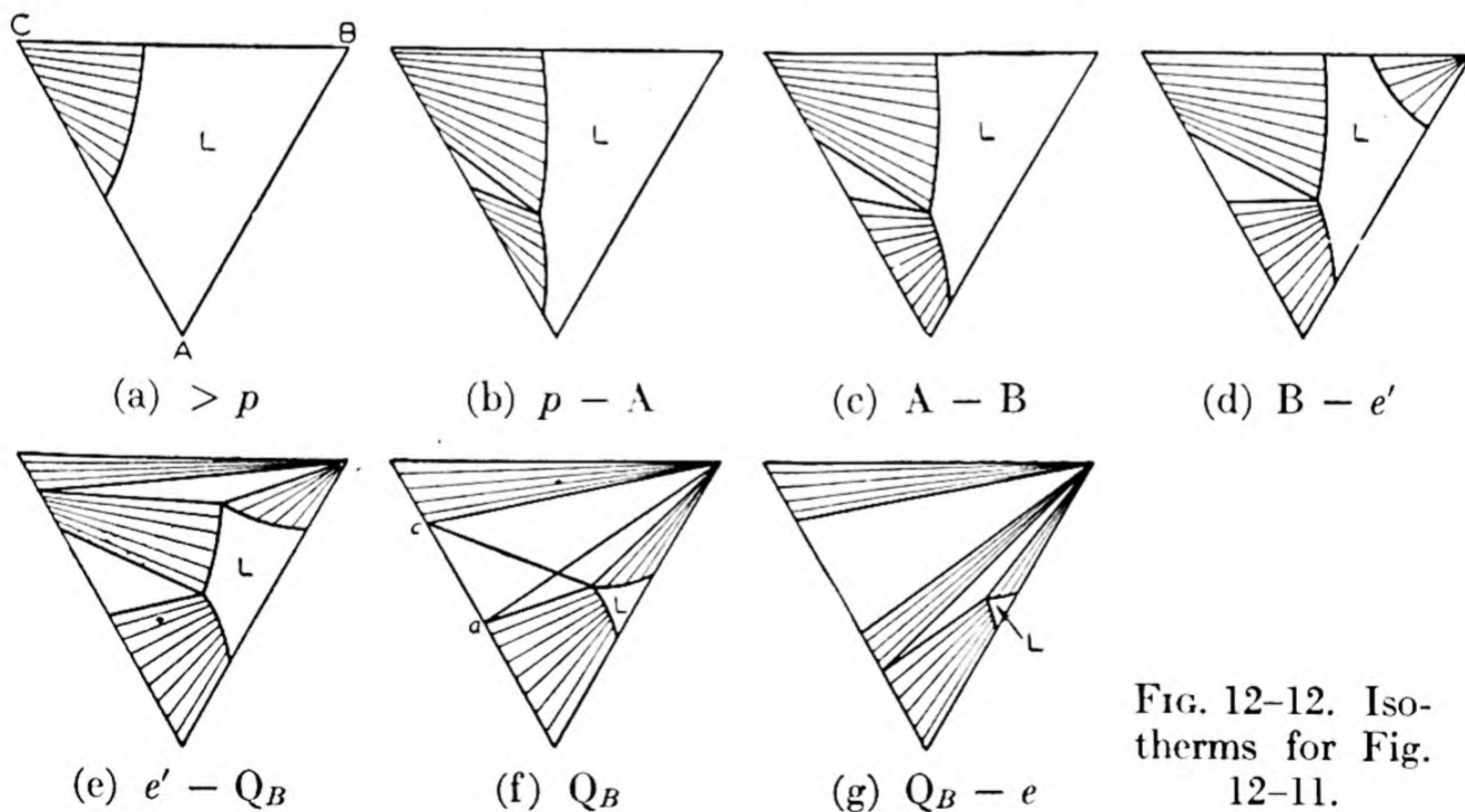


FIG. 12-12. Isotherms for Fig. 12-11.

reaching Q_B . The invariant point is reached only by liquids starting from the quadrangle cBQ_Ba , either traveling on curve $e'Q_B$ (with $\gamma+$, $B+$) or on pQ_B (with $\gamma-$, $\alpha+$). Now those in the triangle cBa solidify completely at

Q_B , losing the liquid phase in the diagonal reaction $L + c \rightarrow B + \alpha + \text{cals.}$; Q_B is thus the incongruent crystallization end-point, for equilibrium solidification, for liquids in aBc . Those in aBQ_B , on the other hand, lose the phase c at the invariant point and then travel on the curve Q_{Be} . This curve is in fact reached by all compositions in aBA . Those in apQ_B reach pQ_B after primary crystallization of γ , move on this curve toward Q_B (without reaching it) until γ is transformed to α , and then leave the curve to travel across the α field to the curve Q_{Be} . Liquids in BQ_{Be} and in ApQ_{Be} reach Q_{Be} directly, after primary crystallization of B or α respectively. When a liquid reaches Q_{Be} , it solidifies before reaching e , to leave $\alpha + B$.

For solidification with effective removal of solid, the systems of Figs. 12-9 and 12-11 are like Figs. 11-24(a) and 11-34 respectively, except that the paths in one field are straight lines.

4. *The MG in the System A-C May Appear or Disappear with Rising T*

a. If the AC binary solid solution is continuous at the binary melting point curve, but meets with falling T , an upper critical solution point at a temperature K , above the eutectic curve ee' of Fig. 12-1, then the liquidus surface $Ce'eA$ of that figure develops a crease at K , which proceeds as a curve of twofold saturation to an intersection with ee' . In Fig. 12-13 the curve is assumed to be similar to $e''E$ of Fig. 12-9 and to reach ee' as an even curve, giving rise to a ternary eutectic E . K' is the composition of the binary AC solid solution at the upper critical solution point, and K and K' are, of course, isothermal. The triangle $\gamma l\alpha$ has as its limits, then, the triangle cEa at the ternary eutectic and the line $K'K$ at the critical solution point. The curve KE is assumed in Fig. 12-13 to be of odd reaction, $l + \alpha \rightarrow \gamma + \text{cals.}$, from K to s , and of even reaction, $l \rightarrow \gamma + \alpha + \text{cals.}$, from s to E . At point s , in other words, the side $l\gamma$ of the 3-phase triangle is tangent to the curve, so that the solids in equilibrium with the liquid s are u and v . The dotted curve $K's$ is the projection of the envelope of the sides $l\gamma$ of the odd-reaction triangles between KK' and vs . The arrows flanking K' indicate the change with falling T in the composition of conjugate solids in equilibrium with liquid on the curve KE . As a curve of even reaction, sE is approached from both sides during crystallization, but the section sK is approached from the A side and is left on the C side.

If the original composition P falls outside the region $K'Ks$ the behavior of the system is exactly as in Fig. 12-9. Liquids in acE must reach E along curve KE . Those on the right of $K'KsE$ reach the curve between s and E , carrying γ , while those on the left of $K'KsE$ reach it anywhere along its length, KE , carrying α ; in either case the curve is followed to point E .

The behavior of liquids with composition in $K'Ks$, when cooled to a tem-

perature below KK' , may be understood by comparison of Fig. 12-13 with Fig. 11-50, which is the same except for the curvature of the curve, here varied for the purpose of illustration. By reference to the discussion of Fig. 11-50 it may be seen that in the present case liquids in $K'Ks$ give α as the primary crystallization product, then $\alpha + \gamma$ while they travel along

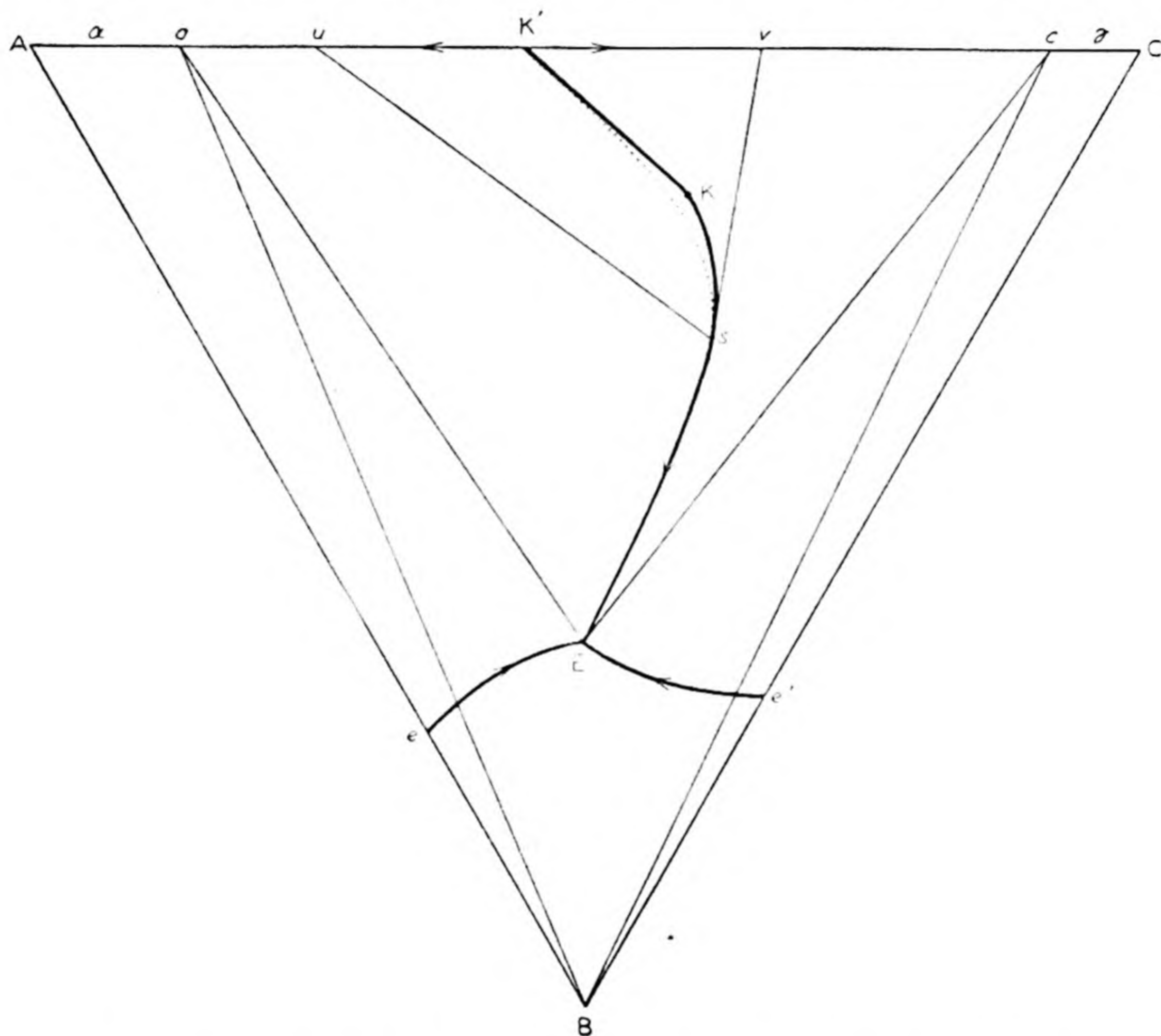


FIG. 12-13. Upper consolute point in AC solid solution.

the curve Ks ; before reaching s they lose the α phase, cross the curve carrying γ alone, and then return again to the curve, below s , to solidify completely at E .

An isotherm above K appears as in Fig. 12-4(b); but as T falls toward K , the tie-lines begin to show an abnormal spreading on the CA base line, and at K they split, the isotherm taking on the appearance of Fig. 12-10(b). The disposition of isothermal tie-lines in such a region may therefore be taken as indicative of positive or negative deviations from ideality in the solid solution. Thus if there is a tendency toward compound formation, for example, the tie-lines are expected to show an abnormal convergence on the solid solution base line.

b. If the $A-C$ system is discontinuous at its melting curve and if its MG becomes closed, at a lower critical solution point, K , above the temperature

of solids for those in pKK' is α , $\alpha + \gamma$, γ , whereupon the liquid leaves the curve on the C side; those in KxK' give α , $\alpha + \gamma$, α , and leave the curve again on its A side. In either case the liquid then continues to the curve ee' to solidify to $B + AC$ solid solution.

B. Pure Components as Solid Phases

The polythermal projection of the liquidus surfaces for this case (Fig. 12-16) on the composition plane (Fig. 12-17) resembles that for three

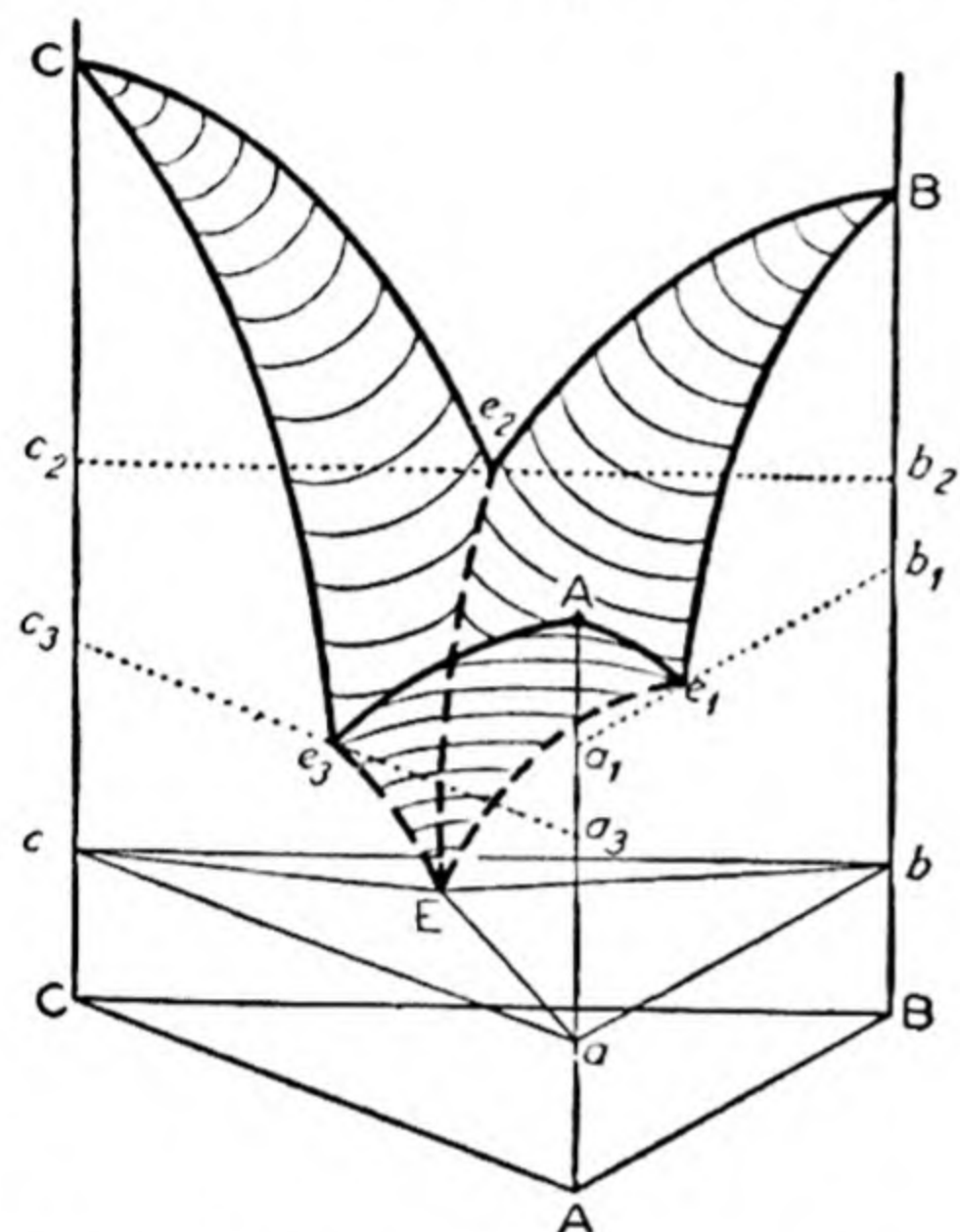


FIG. 12-16. T/c prism for pure solid phases.

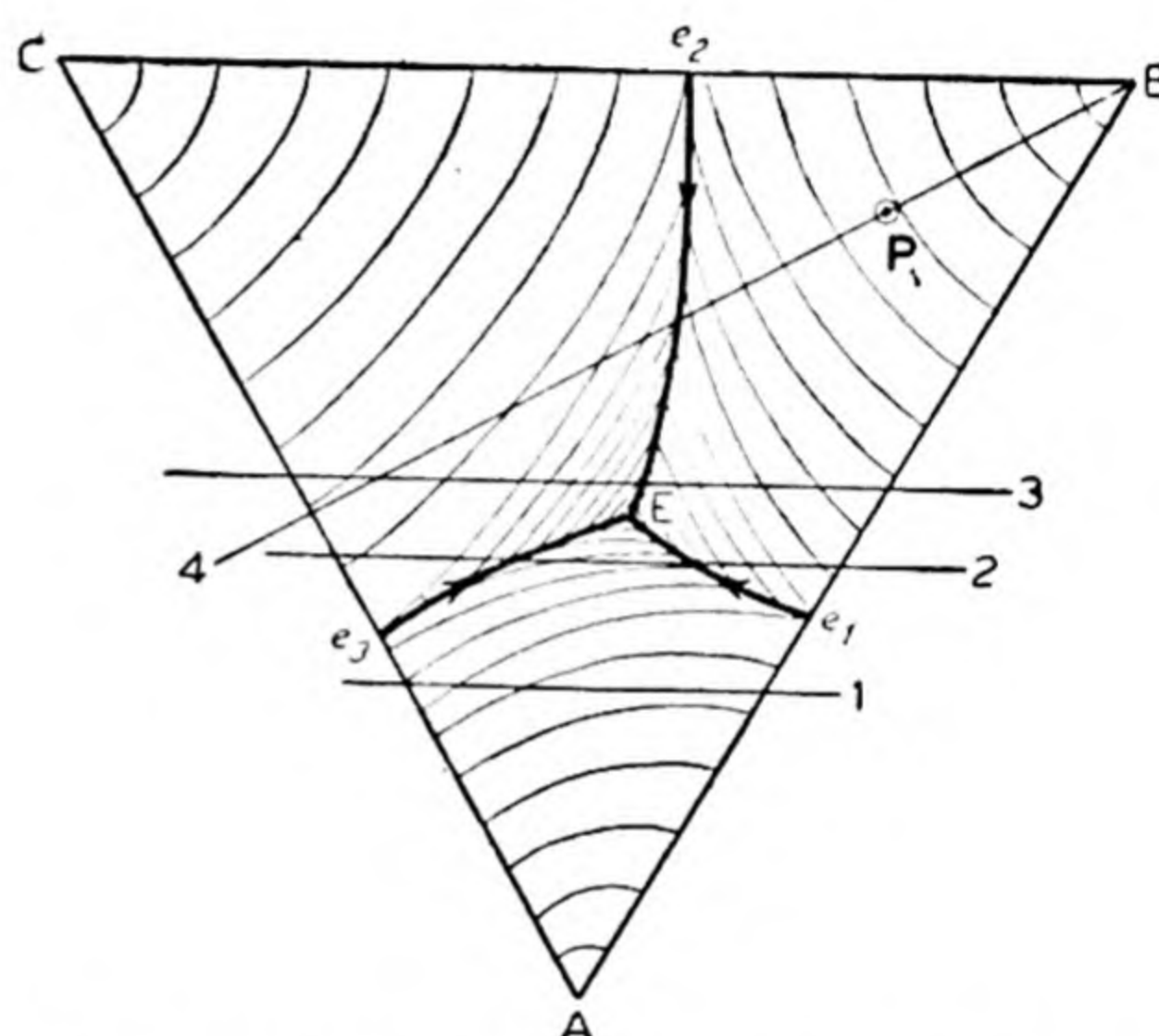


FIG. 12-17. Polythermal projection of Fig. 12-16, showing temperature contours.

separate ternary solid solutions (the case of Fig. 11-21), but the crystallization paths are straight lines (Fig. 12-18). Each liquidus surface is the solubility or freezing surface of a pure phase, so that for the surface Be_1Ee_2 all tie-lines, on any isotherm between B and E, run from the surface to the vertical line B. These tie-lines generate a space, one for each component, of the form of Fig. 12-19,⁵ viewed as in Fig. 12-16 in Fig. 12-19(a), and isothermally, from B toward the side AC, in 12-19(b). The eutectic tie-line $c_2e_2b_2$ enters the prism with falling T as a 3-phase triangle, the phases being C/B, and reaches the eutectic as the triangle cEb of Fig. 12-16.

⁵ See also Masing, (Ref. L), Chapter II.

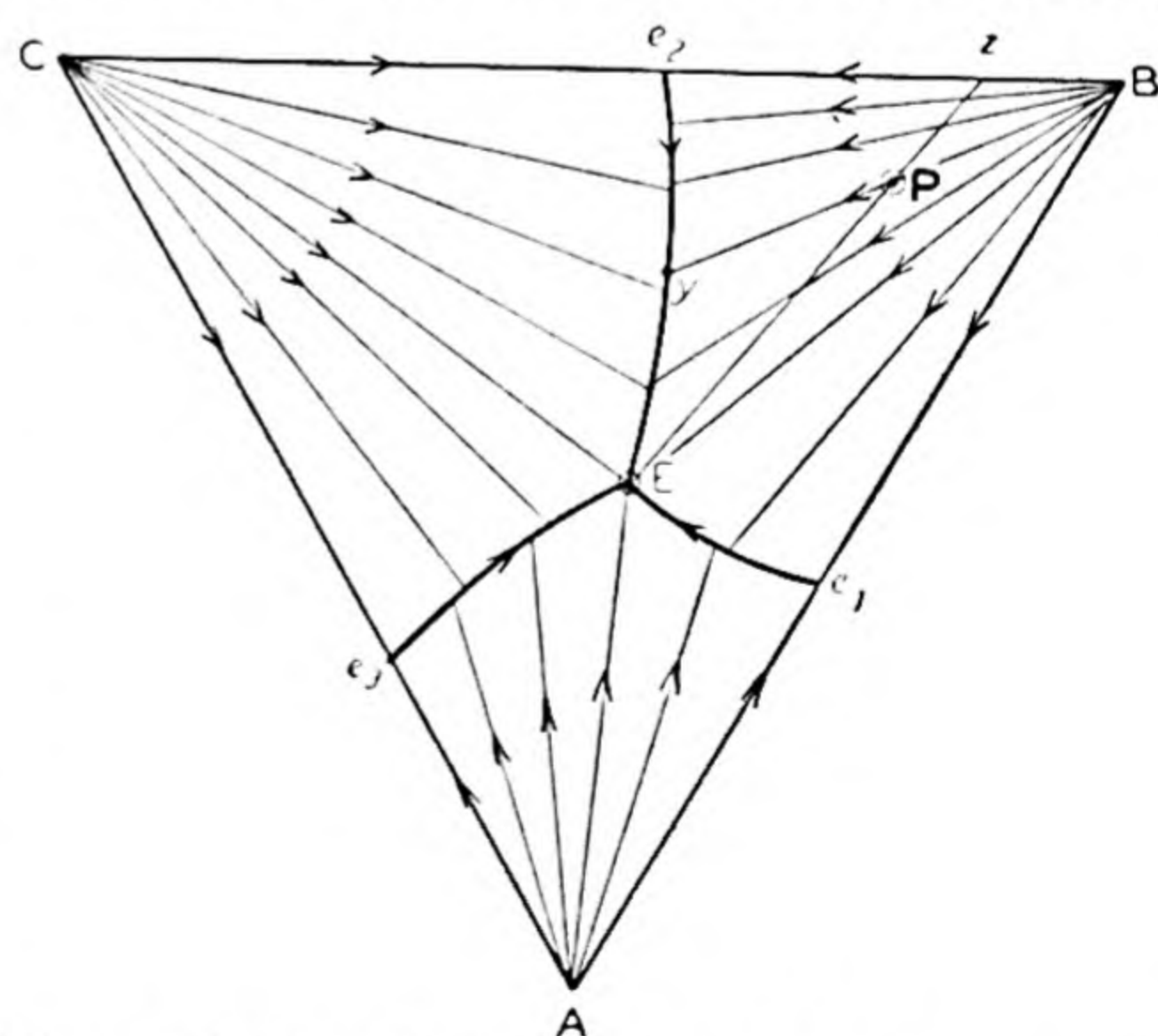
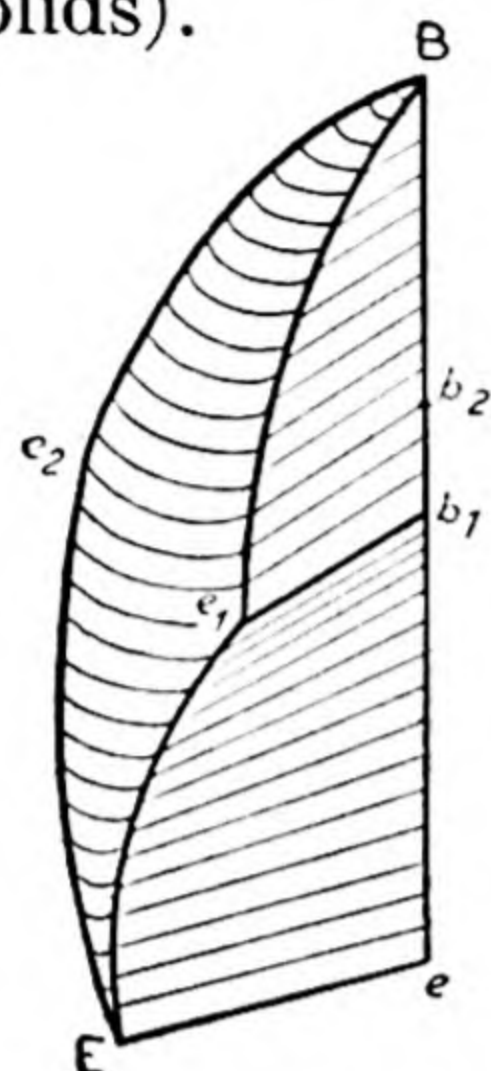
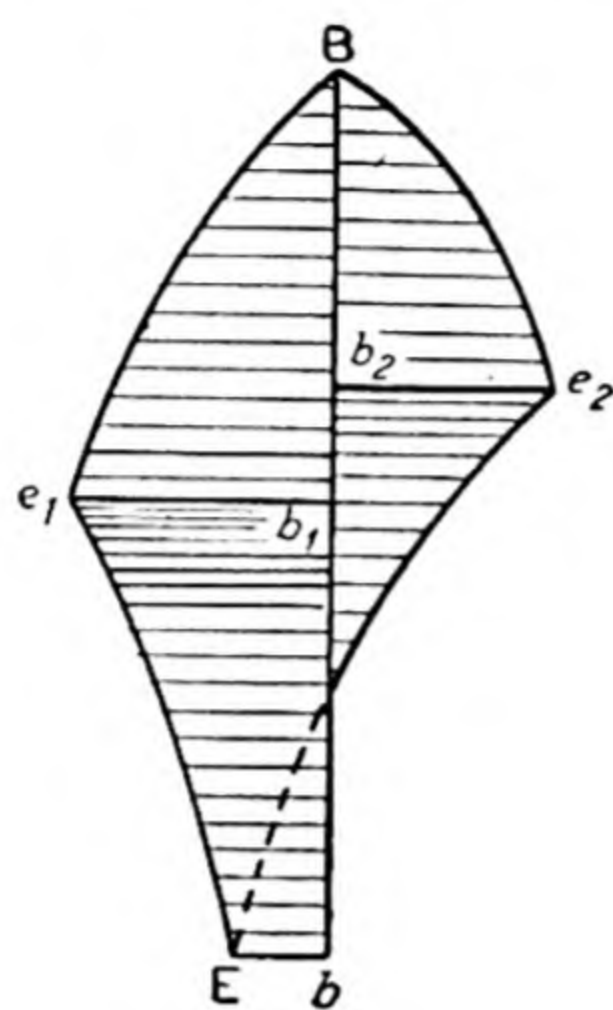


FIG. 12-18. Polythermal projection of Fig. 12-16, showing crystallization paths.

These isothermal triangles generate a space, one for each pair of components, of the form of Fig. 12-20. The plane at E is the 4-phase eutectic equilibrium ABCL, with L at point E. Below E the system is a mixture of $A + B + C$ (solids).

FIG. 12-19. The space $L + B$.FIG. 12-20. The space $L + B + C$.

The vertical sections marked in Fig. 12-17 are shown in Fig. 12-21. Only the uppermost curve of these sections is the cut of a solubility surface; the others are points on tie-lines. The isotherms, assuming $C > B > e_2 > A > e_1 > e_3 > E$, are shown in Fig. 12-22. Fig. 12-22(c) is typical for the system solvent (liquid A) and two pure components as sole solid phases.

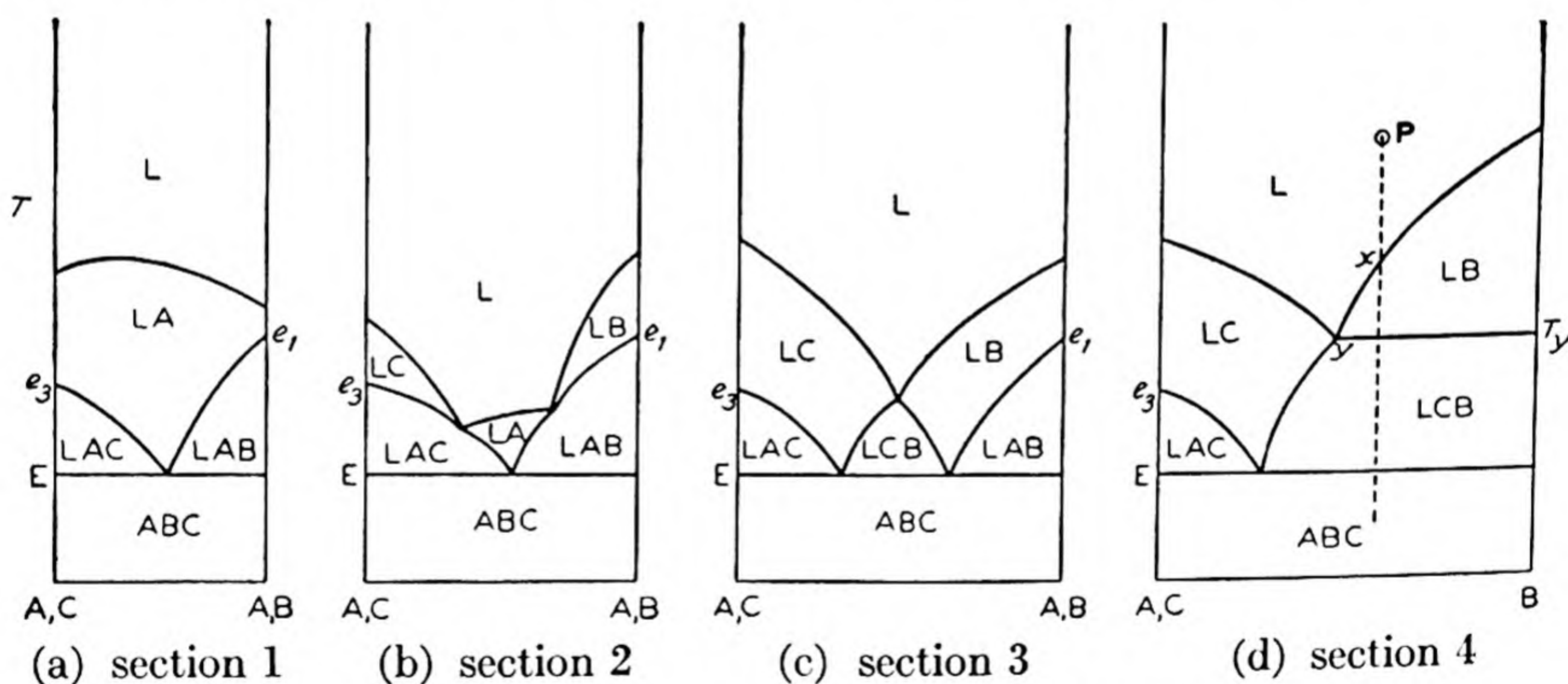


FIG. 12-21. Vertical sections of Figs. 12-16 and 12-17.

When the only solid phases are the pure components, every ternary liquid reaches the ternary eutectic before complete solidification, whether or not the solid is "effectively removed" during solidification, for the only final possibility is a mixture of all three solids. Hence any liquid with composition P in the B field of Fig. 12-18 produces solid B , in primary crystallization, when cooled to the surface Be_2Ee_1 of Fig. 12-16. If Fig.

12-21(4) represents the vertical section through the points **P** and **B**, then the temperature at which the liquid reaches the surface is given by point x . This is the first break in the cooling curve of liquid **P**, which would be like that of Fig. 11-23(c). The liquid composition then moves on the **B** surface on a path (straight line in polythermal projection) away from **B** and, in the present case, reaches the eutectic curve e_2E ; the composition of the liquid at

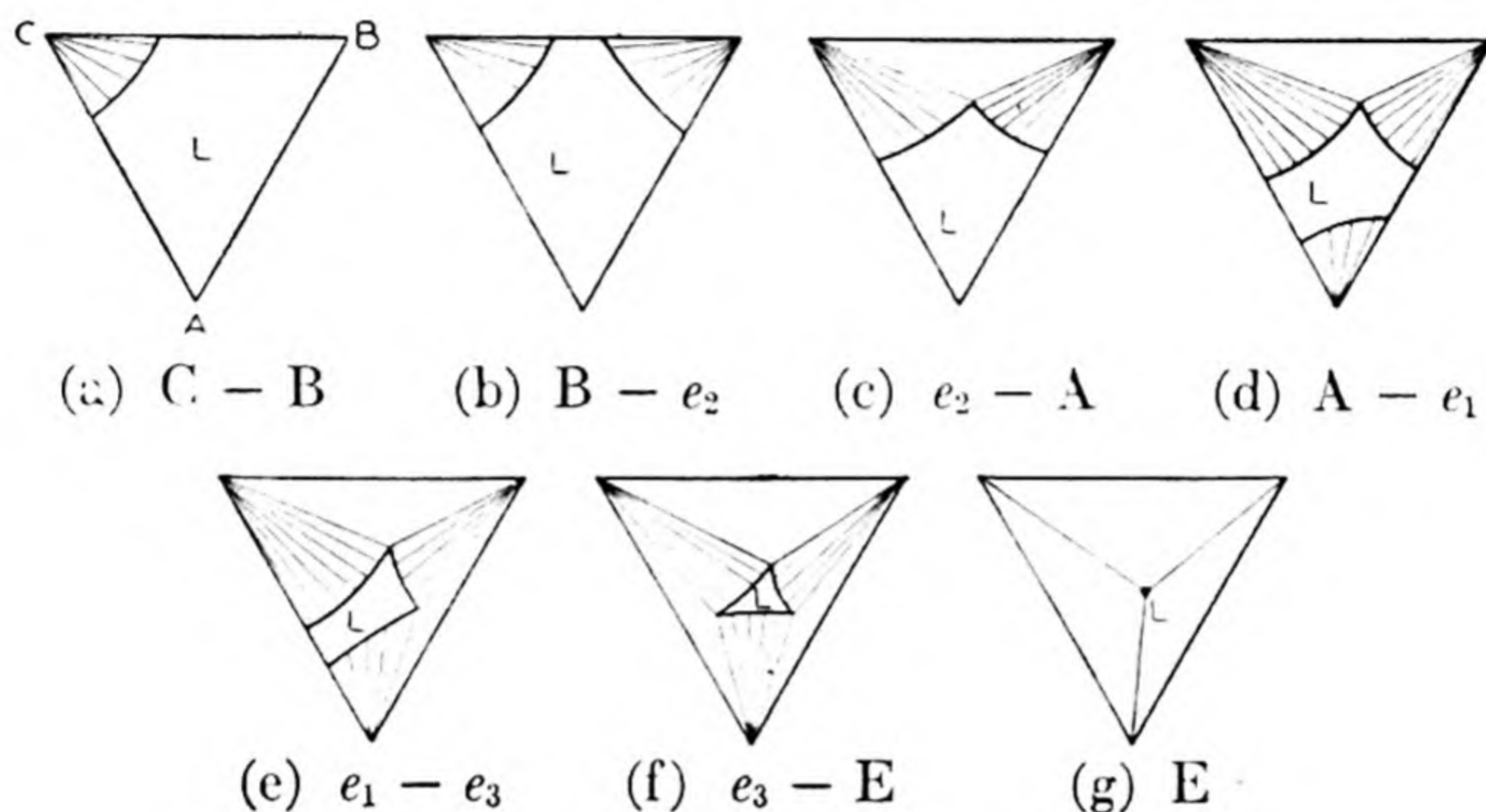


FIG. 12-22. Isotherms of Fig. 12-16.

this point is given by y of Fig. 12-18, and the temperature by T_y of Fig. 12-21(4). This is the break marking the start of the secondary crystallization ($B + C$) in the cooling curve. The quantity of **B** crystallized when this point is reached may be calculated from the segments of the tie-line yPB of Fig. 12-18: $B/y = Py/PB$. During the secondary crystallization the liquid composition moves on the curve e_2E toward **E**, and when **E** is reached the residual liquid solidifies isothermally to a mixture $A + B + C$, the duration of the temperature halt depending on the quantity of liquid reaching **E**. If the quantity of liquid reaching y was calculated, the quantity of material solidifying as secondary crystallization may be calculated by means of the line Ey extended to a point w (not shown) on **CB**; $(C + B)$, secondary, $/E = Ey/yw$. In terms of separate phases, $(C + \text{total } B)/E = EP/Pz$, and $C/B = zB/Cz$. When solidification is complete, the relative proportions of the three phases are, of course, those of the composition **P** itself. It is also possible to calculate the composition of the mixed solids if the eutectic crystallization is stopped at any point, leaving a known amount of liquid, since the proportions of the three solids produced from the eutectic liquid are those of **E** itself.⁶

⁶ On thermal analysis of ternary systems, see R. v. Sahmen and A. v. Vegesack, *Z. phys. Chem.*, **59**, 257 (1907); also R. Vogel (Ref. V), pp. 375-380. For an elaborate example of the application of thermal analysis, see the system **Pb-Zn-Sb**, R. Loebe, *Metallurgie*, **8**, 7 (1911); but for later work on this system, see G. Tammann and O. Dahl, *Z. anorg. Chem.*, **144**, 1 (1925).

C. Binary Compounds

Since the faces of the T/c prism are the isobaric sections of the individual binary systems, the only binary compounds which may appear as stable phases in the solid-liquid equilibria of the ternary system are those which are stable in the binary systems at the pressure of the prism and at temperatures above the lowest ternary eutectic. A binary compound in stable solid-liquid equilibrium in its own binary system, such as the compounds D_2 , D_3 , D_4 and D_5 of Fig. 12-23, always appears, with its own crystalliza-

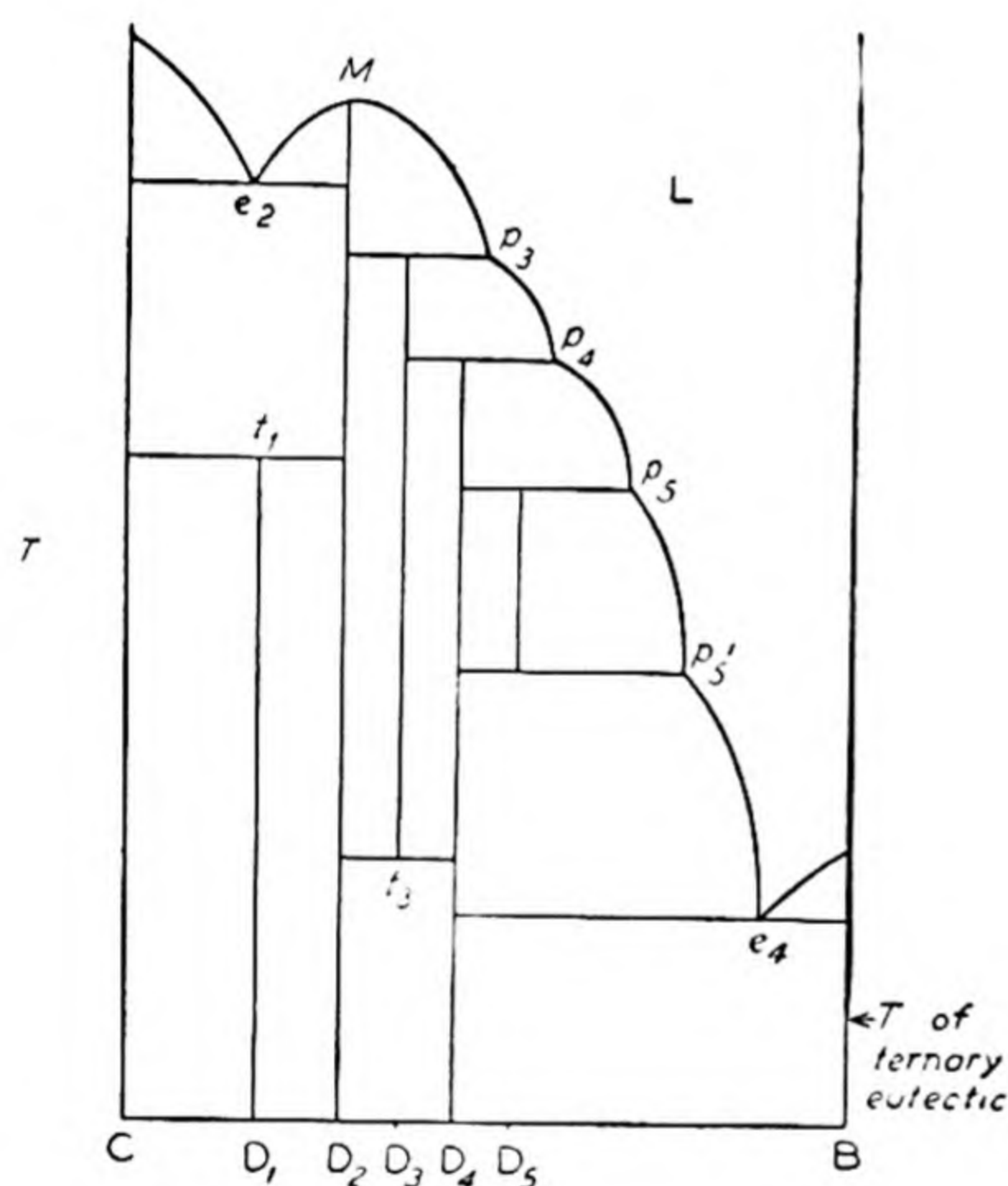


FIG. 12-23. Types of binary compounds.

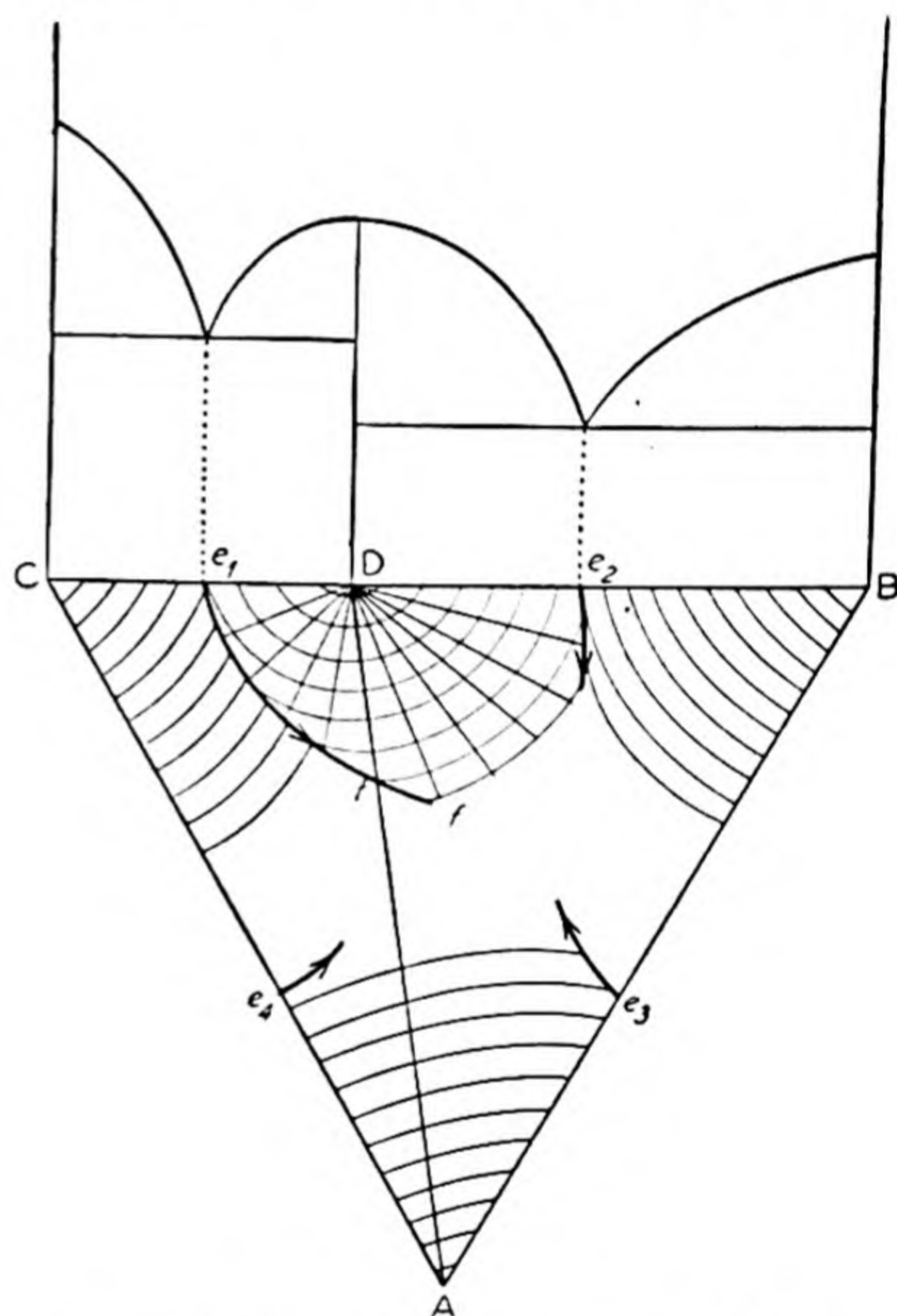


FIG. 12-24. Congruently melting binary compound.

tion surface, in the ternary system. But a binary compound such as D_1 of Fig 12-23, which can exist at the pressure and in the T -range just specified, but which does not reach the binary melting point curve, may or may not show itself in the ternary crystallization surface. If it does, then its crystallization field or surface will lie entirely inside the composition triangle, not touching any side, and it appears, with decreasing T , at a T not above t_1 . The compound D_5 , with an upper and lower transition temperature in equilibrium with binary liquid, has a crystallization field bordering on the AB side, the field being stable between the temperature limits p_5 and p'_5 . The crystallization fields for D_2 , D_3 , and D_4 , also bordering on the side AB, start at the temperatures M , p_3 , and p_4 , respectively; the lower temperature

limits of the D_2 and D_4 fields cannot be predicted if they are still stable below the lowest ternary eutectic, but that of D_3 must be not below t_3 .

Each of the binary invariant points e_2 , p_3 , p_4 , p_5 , p'_5 , and e_4 is the origin of a curve of two old saturated liquid entering the prism, and dividing the ternary liquidus into various crystallization fields or surfaces. Since we shall assume in this section that the binary compounds form no solid solutions, the curves from points such as e_2 , p_3 , p_4 , and e_4 are curves of falling T through their entire course. That from p_5 also falls, while that from p'_5 (an "inverse peritectic"; cf. Fig. 7-19) rises in T , and the two may join as a continuous curve. The curves from e_2 and e_4 start as curves of even crystallization ($++$), the others as curves of odd reaction; but as explained in Chapter XI, Fig. 11-3(b), the reaction of any curve may change at some point in its ternary course.

We shall first consider a compound stable from the binary melting curve to temperatures below the ternary eutectic, and which may be congruently or incongruently melting.

1. *Congruently Melting Binary Compound (Fig. 12-24)*

The point D, representing the composition of the compound, is the maximum temperature in the D field and is on the boundary of the field, being a point on the edge e_1e_2 . Any ternary liquid with composition in this field precipitates D when cooled to the crystallization surface, and as D is precipitated the composition of the residual liquid moves in a straight line — on the polythermal projection — away from the point D, eventually reaching a curve of twofold saturation, such as the eutectic curves originating at e_1 and e_2 or some third curve connecting these. Any one of the isothermal contours on this projection, concentric around D in the D field, is an isothermal solubility curve of D in the ternary system. Between the temperatures D and t , where the curve e_1f is shown crossing the line DA, each of these isothermal solubility curves is cut by the line DA. The compound is then said to be **congruently soluble in A**, in this temperature range. In the range below t , when its isothermal solubility curve is not cut by the line DA, it is said to be **incongruently soluble in A**. A congruently melting binary compound always has some range of congruent solubility, starting from its melting point. The curve e_1f may, of course, end at some isobaric 4-phase invariant point, intersecting two other curves, before reaching the line DA. Also, it may or may not change to a curve of odd reaction either above or below t .

As for the two invariant points to be produced by the intersection of the four curves of twofold saturation, we first observe that when the ternary liquid is completely solidified, the system consists of three solids, which

must be either $C + D + A$ or $D + B + A$, each set of coexisting equilibrium solids defining a sub-triangle of the diagram. If the two invariants occur one in each of these sub-triangles, they are both ternary eutectics. If they are both in the same triangle, one is a ternary eutectic, the other a ternary peritectic. The eutectic solution lies inside the triangle of the three solid phases saturating it, three curves of even reaction fall to it, and it is a congruent crystallization end-point for compositions in its triangle. The peritectic solution lies outside its triangle; at least one of its curves falls away from it in temperature, and it acts as the incongruent crystallization end-point for (the equilibrium solidification of) liquids with original compositions within the triangle of its three solids. The combination of the three binary systems of Fig. 12-24 therefore has three possibilities: Fig. 12-25, in which (b) and (c) are the same general case except for position.

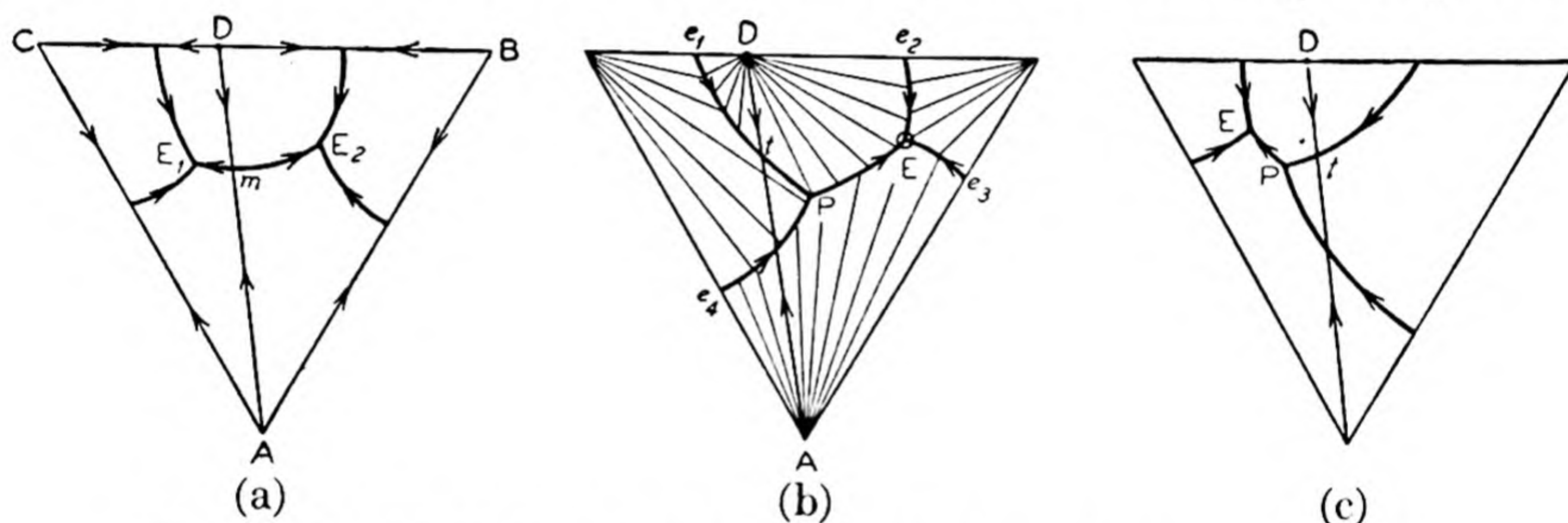


FIG. 12-25. Variations for congruently melting binary compound.

In each case the connecting curve, E_1E_2 or PE , is a liquid in equilibrium with A and D , since it is the intersection of the solubility surfaces of D and A , or the common boundary of their fields.

The invariants in 12-25(a) are both eutectics, and hence the temperature on E_1E_2 must be a maximum at point m , falling from m toward each eutectic. This maximum, a **saddle point** on the eutectic curve E_1E_2 , lies on the line DA , since the reaction on the curve E_1E_2 is $L \rightarrow D + A + \text{cals.}$ on either side of m ; m is at the same time the minimum on the section DA (Figs. 12-26 and 12-27). The system $\text{Na}_2\text{SO}_4\text{--NaF--NaCl}$, with the compound $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$, illustrates Fig. 12-26. The system of Fig. 12-25(a) may therefore be considered, in respect to the condensed phases involved, as two separate simple ternary systems, $C\text{--}D\text{--}A$ and $D\text{--}B\text{--}A$ (except for the shape of the D surface, especially near the congruent melting point of D), and the vertical section DA (Fig. 12-27) is known as a **quasi-binary section**. D is seen to be congruently soluble in A from D to m ; it is never incongruently soluble in A . The contours and crystallization paths in the D field are shown in Fig. 12-28, and some isotherms in Fig. 12-29.

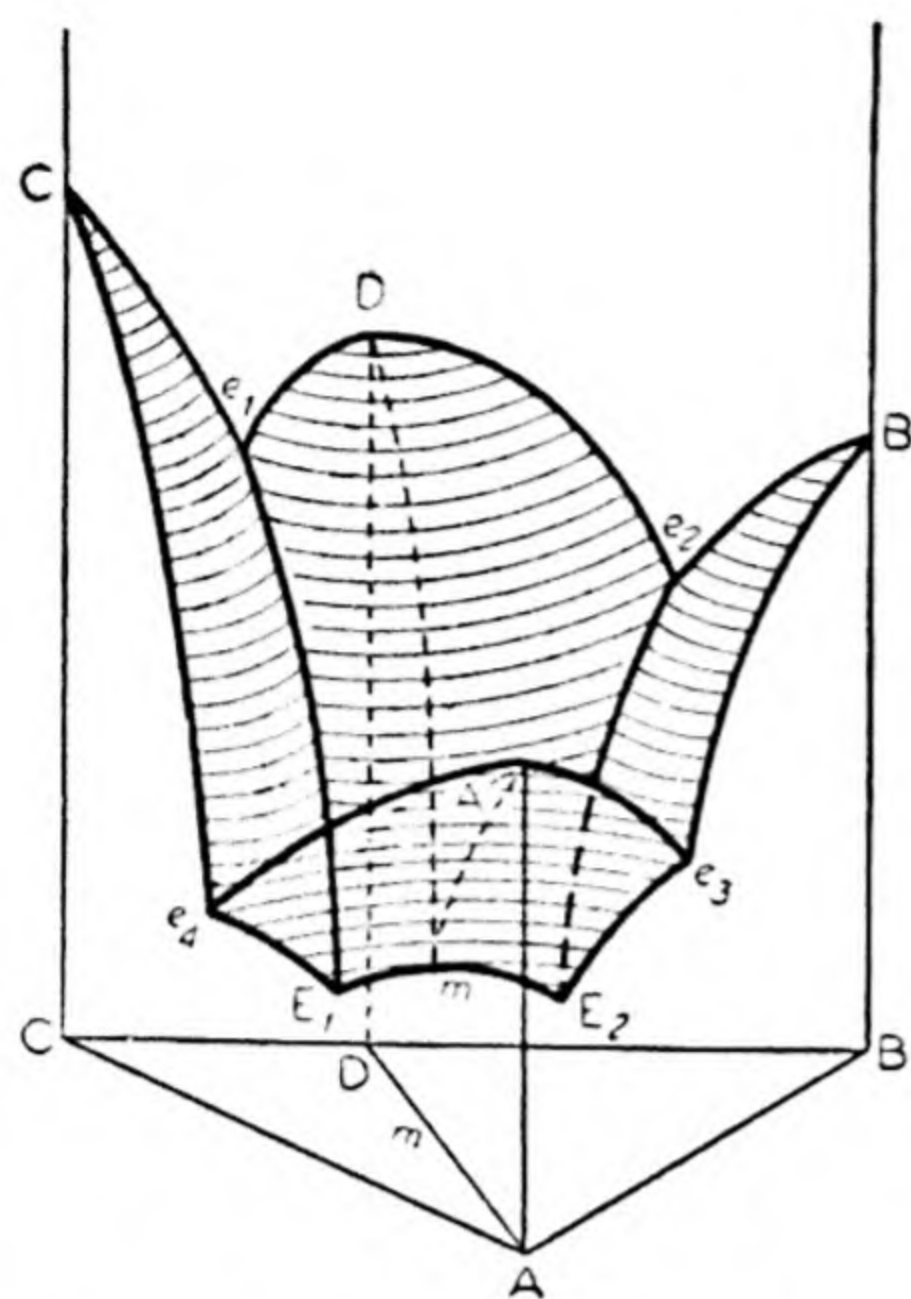


FIG. 12-26. T/c prism for Fig. 12-25(a).

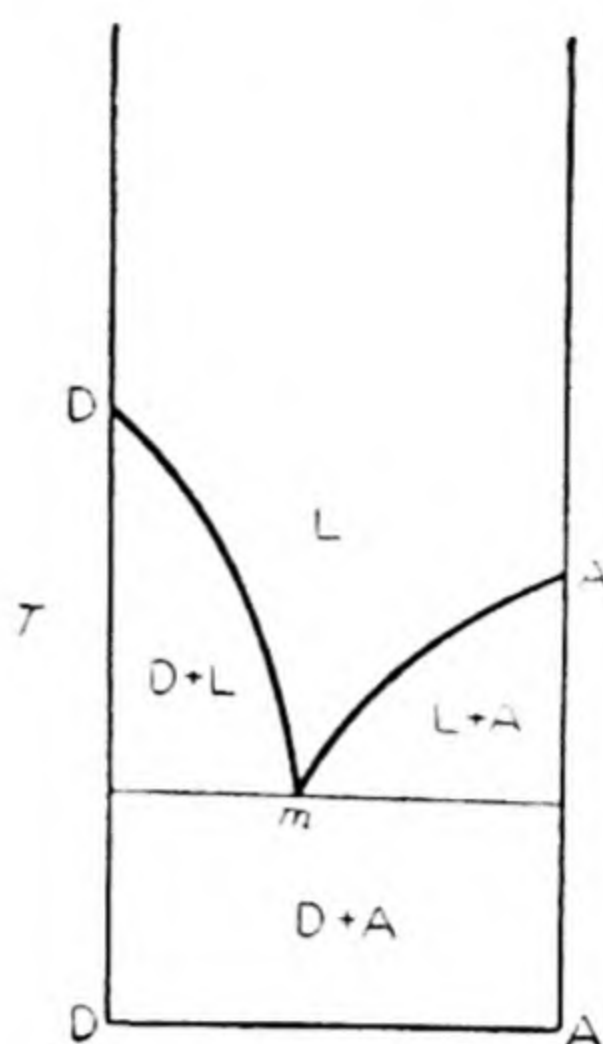


FIG. 12-27. Section DmA of Fig. 12-26.

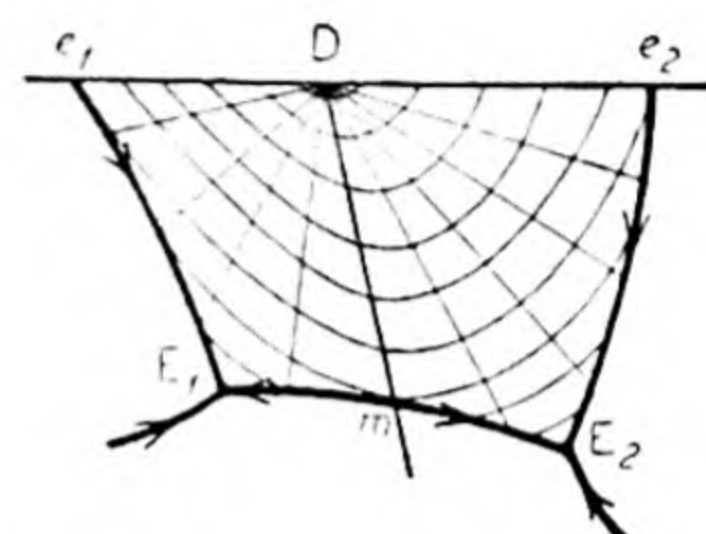
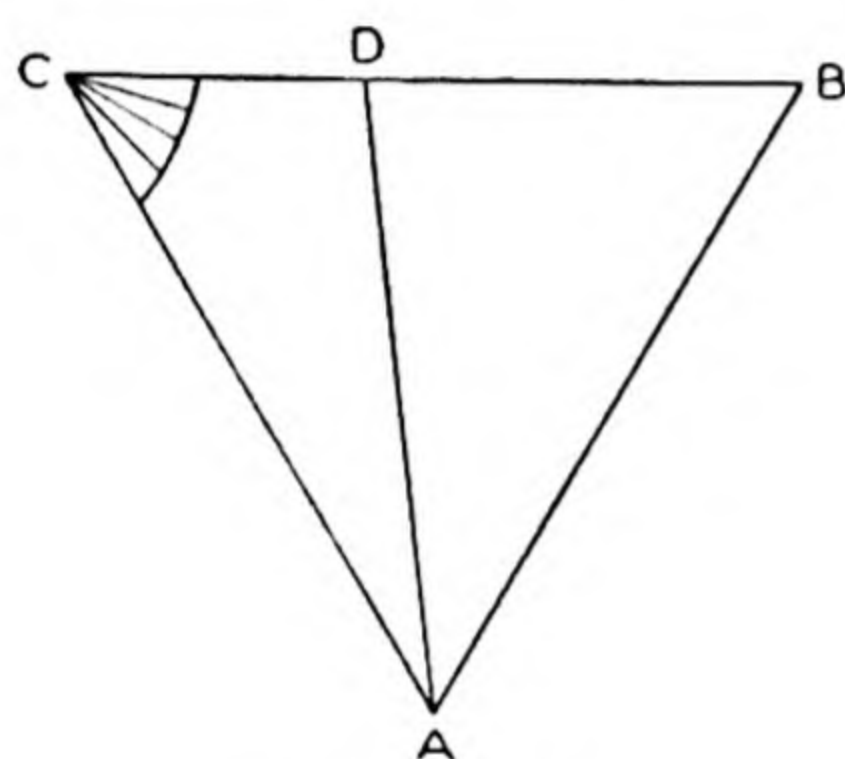
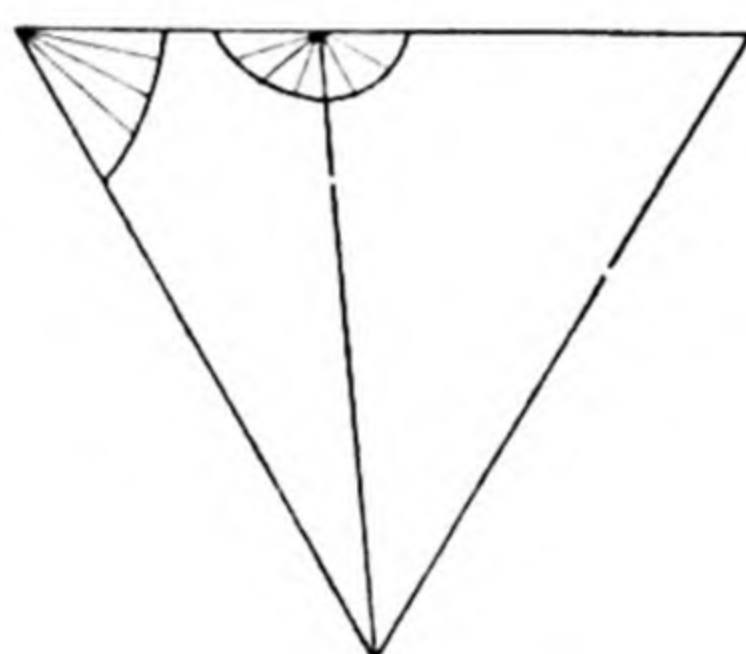


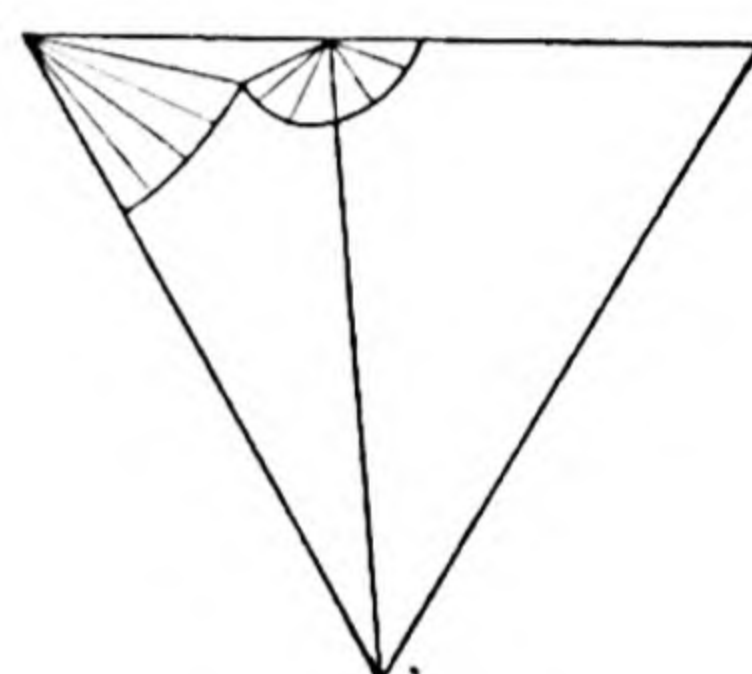
FIG. 12-28. The D field of Fig. 12-26.



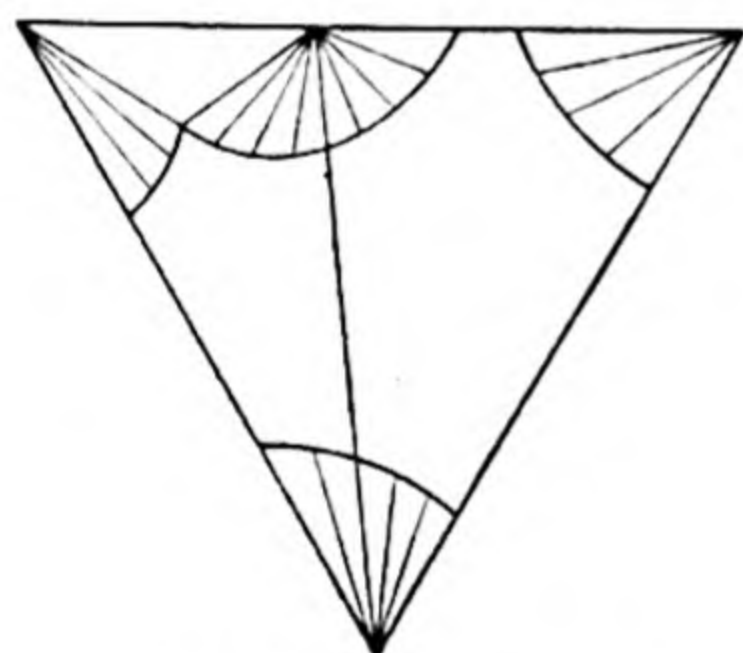
(a) C - D



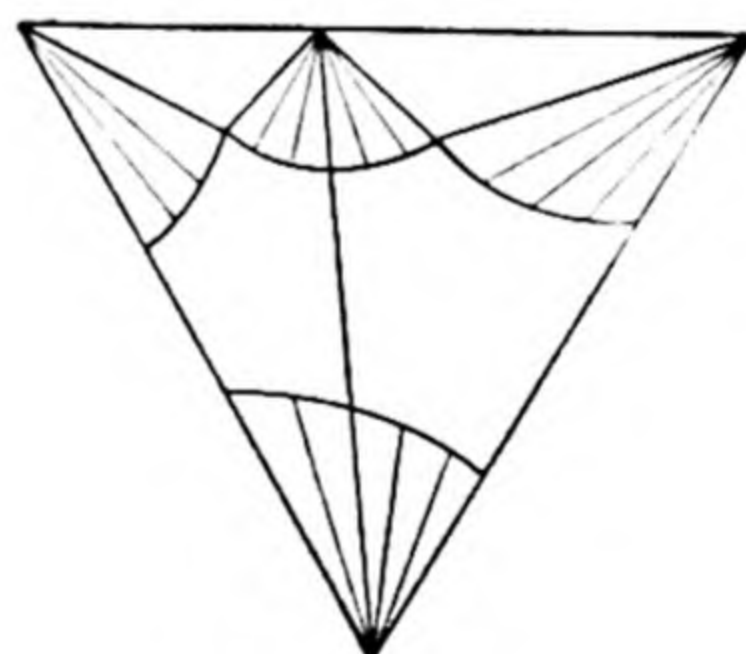
(b) D - e_1



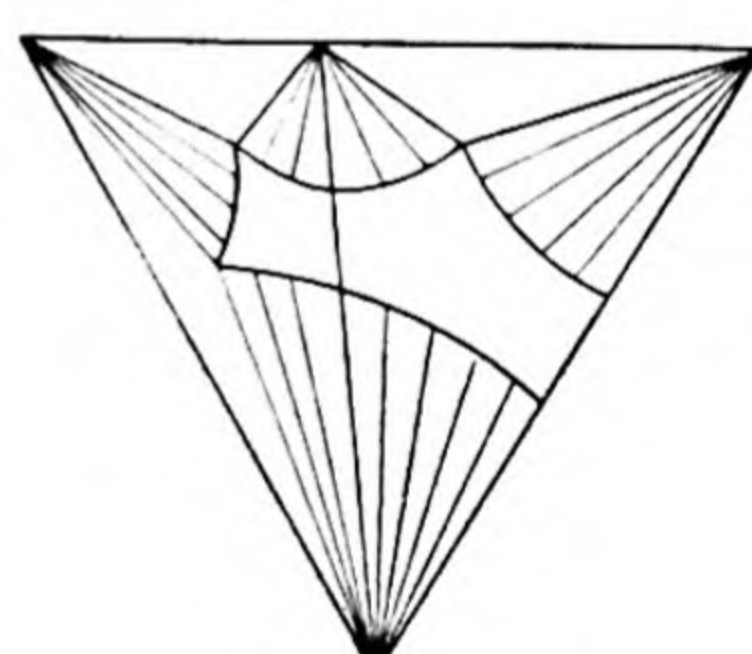
(c) e_1 - B



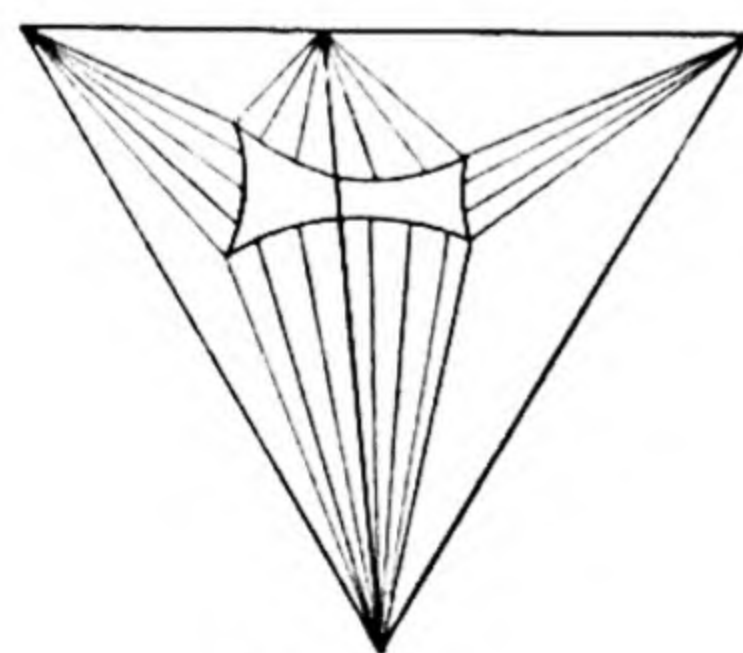
(d) A, B - e_2



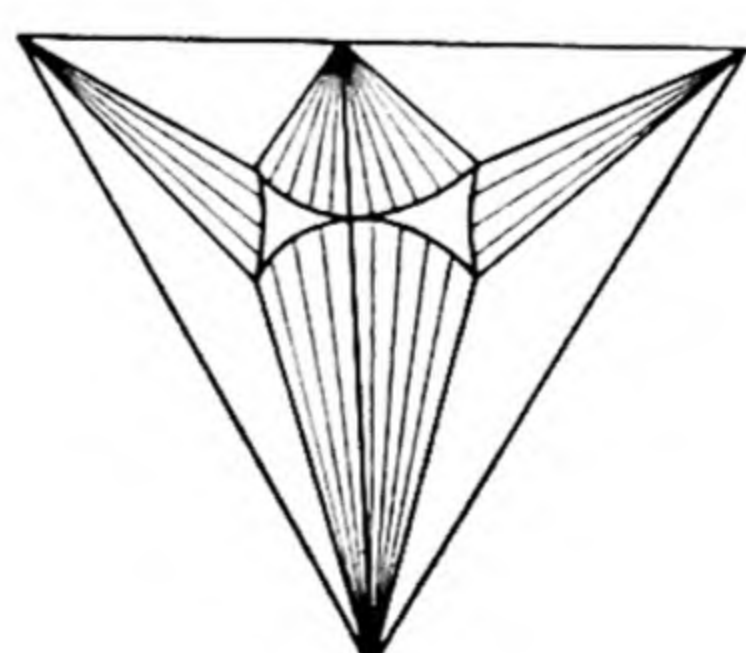
(e) e_2 - e_4



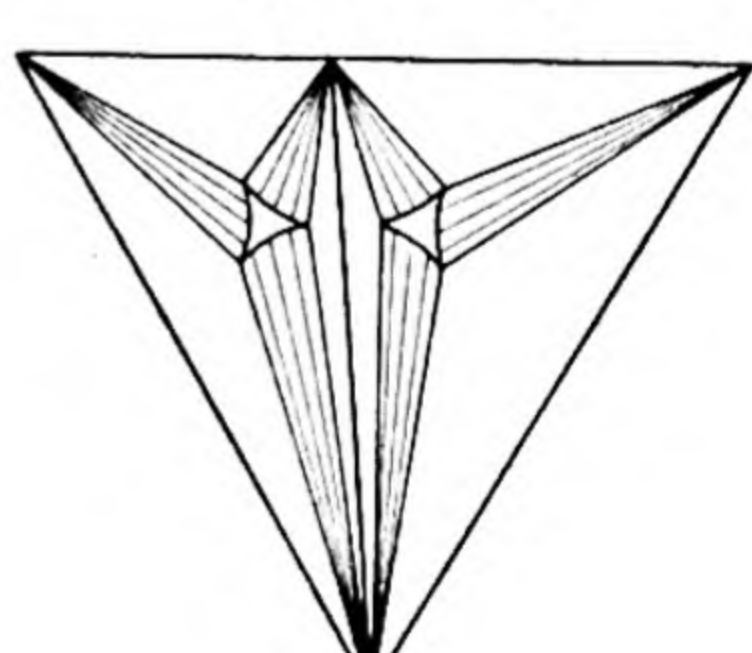
(f) e_4 - e_3



(g) e_3 - m



(h) m



(i) $< m$

FIG. 12-29. Isotherms of Fig. 12-26, with $e_4 > e_3$.

In Fig. 12-25(b) there is no quasi-binary section, since D is incongruently soluble in A below the temperature t . As drawn, the three curves intersecting at P are all of even reaction, but P is not a eutectic since T falls from P to E. Liquids in the triangle CPA reach P on the curve e_4P , carrying the solids C and A; liquids in the triangle CDP reach P on the curve e_1P ,

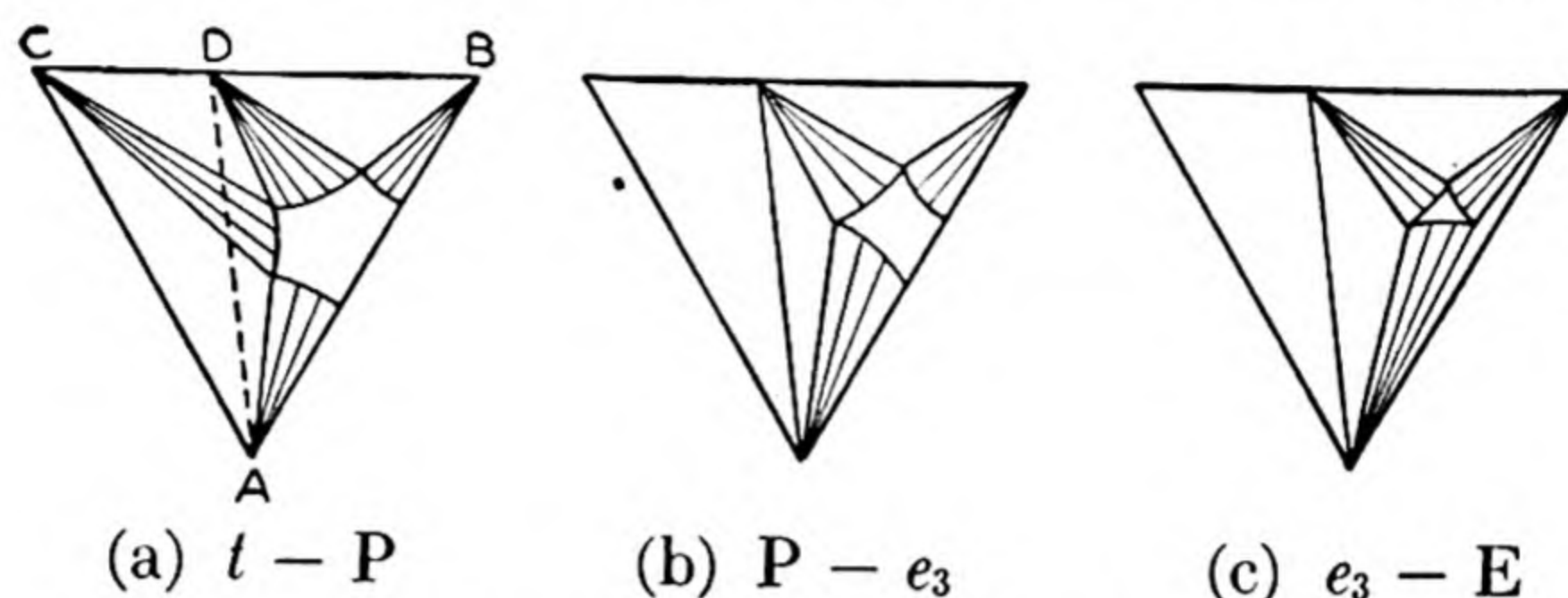


FIG. 12-30. Isotherms of Fig. 12-25(b).

with the solids C and D. At P the system is invariant, the (diagonal, type B) reaction being $L + C \rightarrow A + D + \text{cals.}$ If the total composition lies in the triangle CDA, the liquid is consumed, and P is the incongruent crystallization end-point; otherwise C is consumed, and the liquid, precipitating D and A, proceeds to the eutectic E. The relations at point P of this system are analogous to those in the system of Figs. 11-28 to 11-30,

in which also three even curves give rise to a peritectic, quadrangular reaction.

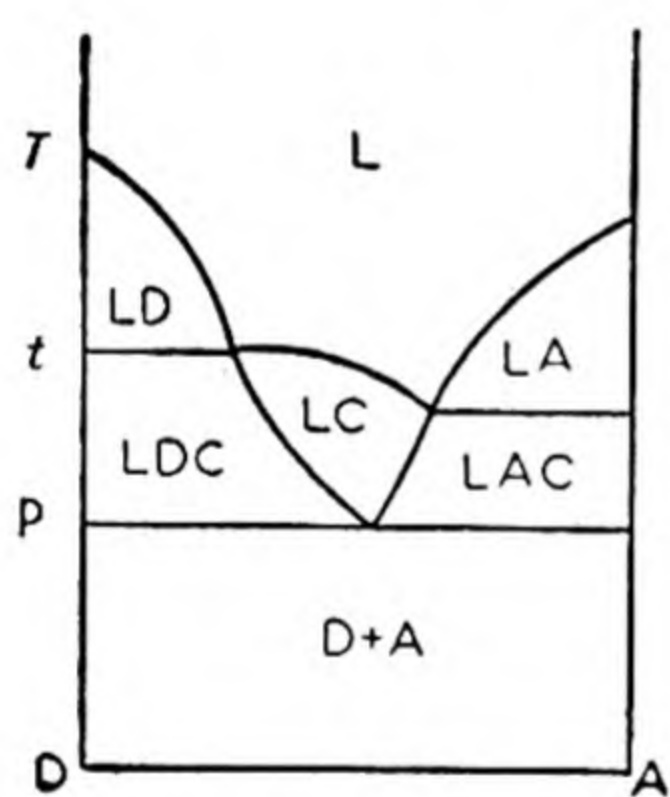


FIG. 12-31. Section DA of Fig. 12-25(b).

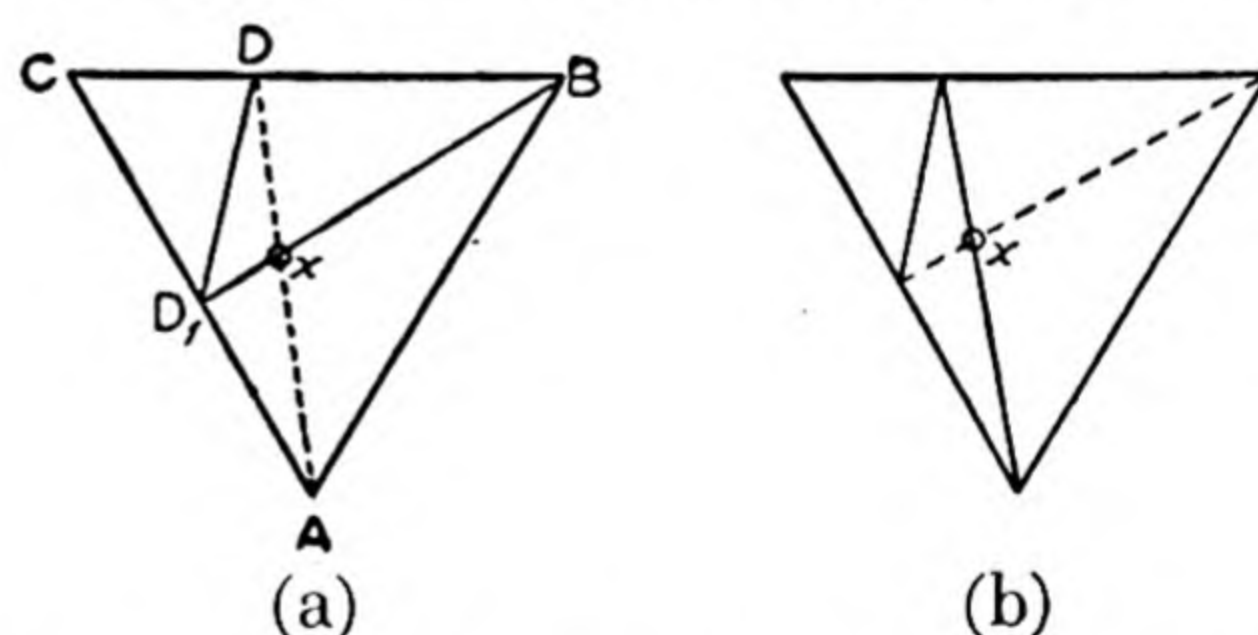


FIG. 12-32. Guertler's "Klärkreuzverfahren," simple case.

Isotherms above the temperature t would be similar to those shown in Fig. 12-29(a-f); others are shown in Fig. 12-30. Fig. 12-31, the vertical section DA, is to be compared with Fig. 12-27. In the present case a liquid with composition on the line DA will give, on complete solidification, a mixture of D and A only if C is given time to redissolve at point P (the line P of Fig. 12-31). Otherwise it proceeds to E to leave a mixture of all four solids.

If the system contains a number of binary compounds, whether congruently or incongruently melting, there will be a number of ways in which the ABC triangle may be divided for the possible 3-solid mixtures resulting when ternary liquid is cooled to complete (equilibrium) solidification, instead

of the single possible division of Fig. 12-25, unless the compounds are all in one binary system. With the two compounds D and D_1 of Fig. 12-32, for example, there are two arrangements of three 3-solid triangles possible. Which arrangement applies to a given ternary system cannot be predicted from the three separate binary diagrams. But the investigation of the ternary relations would be facilitated if the fundamental arrangement could be known beforehand. If a liquid with composition x , at the crossing of the possible diagonals DA and D_1B , is cooled to complete solidification, the arrangement is (a) if the only solid phases produced are $D_1 + B$, and (b) if they are $D + A$. The method, known as Guertler's "*Klärkreuzverfahren*,"⁷ is dependable if the section through x is quasi-binary. It will otherwise generally fail because of the difficulty of maintaining complete equilibrium throughout the solidification; but it is nevertheless potentially always a valuable experiment.⁸ Whichever arrangement applies, there will be three invariants, for two binary compounds; if there is one quasi-binary section, there are at least two eutectics, etc. In the case of Fig. 12-33, involving three compounds, there are three

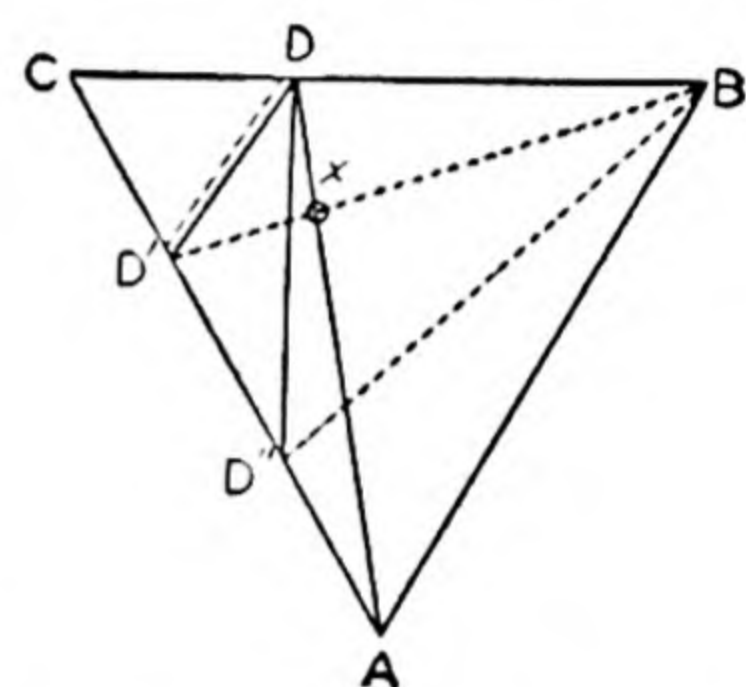


FIG. 12-33. Case of three binary compounds.

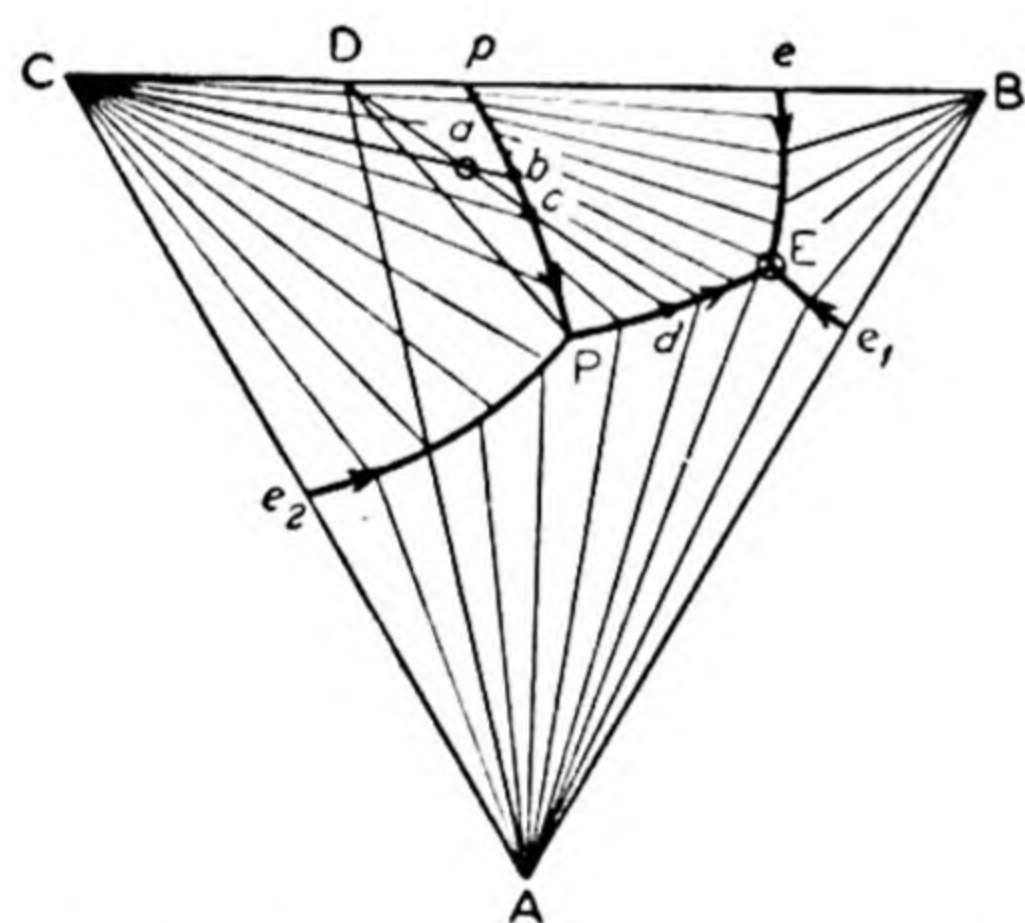


FIG. 12-34. Incongruently melting binary compound.

possible arrangements of the solid phases. Theoretically, a single experiment with the composition x suffices to establish which of the three arrangements prevails, for the equilibrium solids obtained from liquid x will be $A + D$ if the arrangement is that of the solid lines, $D' + B$ if it is that of the dotted lines, and $B + D + D''$ if the lines involved are $D'-D-D''-B$.

2. Incongruently Melting Binary Compound

The point D (Fig. 12-34), representing the composition of the compound, now lies outside the D field, but it is nevertheless the point of origin of the crystallization paths in its field. Some isotherms are shown in Fig. 12-35, which may be considered followed by Figs. 12-30(b) and (c).

⁷ W. Guertler, *Metall. und Erz*, **8**, 192 (1920).

⁸ The determination of what may be called the crucial composition (point x for the system of Fig. 12-32 (a, b)) is very simple in the ternary case. For the corresponding problem for systems of higher order, see the paper, "Co-existence relations of $n + 1$ phases in n -component systems," P. M. Pepper, *J. Applied Physics*, **20**, 751 (1919).

Liquids in CPA (Fig. 12-34) reach P on e_2P , with solids C and A; liquids in CDP reach P on pP with C and D. At P, the invariant reaction, $L + C \rightarrow A + D + \text{cals.}$, proceeds until, for those in CDA, liquid is consumed leaving $C + D + A$, or, for those in DPA, until C is consumed, whereupon the liquid, precipitating D and A, moves to E.

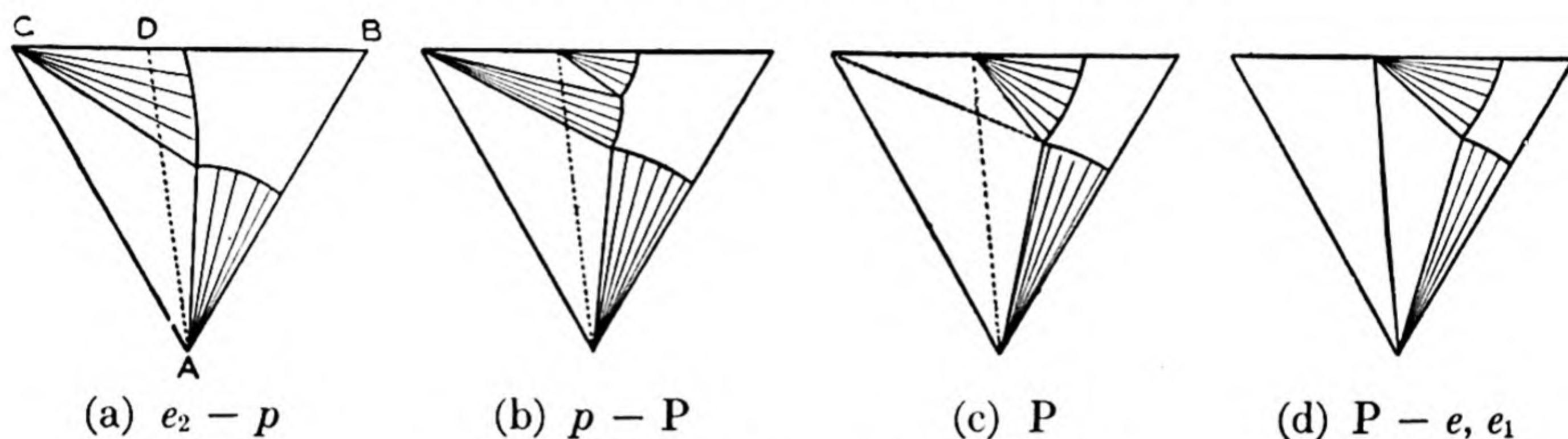


FIG. 12-35. Isotherms of Fig. 12-34.

Liquids in DpP give C as primary product and reach the curve pP . Thus for the original liquid a , this curve is reached at b . When D begins to form (reaction, $L + C \rightarrow D + \text{cals.}$), the liquid moves on the curve toward P, and the solid, now a mixture of C and D, moves on the line CD toward D. The tie-line joining solid (or mixture of two solids) with the liquid must always pass through point a . Hence when all C has been transformed to D, the liquid lies on point c . Saturated now only with D, the liquid leaves the curve on a crystallization path leading away from D across the D field, that is, the extension of line Dac . It finally reaches the curve PE at point d , when A begins to form. As the liquid now moves to E, the composition

of the solid mixture ($D + A$) is given by the line joining the liquid on the curve PE and point a , extended to the line DA. The process continues as discussed for eutectic solidification, under Part B.

These relations also hold for the region Dtp of Fig. 12-36. In this diagram the incongruently melting compound becomes congruently soluble in A, at the temperature of point t . The curve originating at the binary peritectic p is one of odd reaction ($L + C \rightarrow D + \text{cals.}$) from p to point s , where the line Ds is

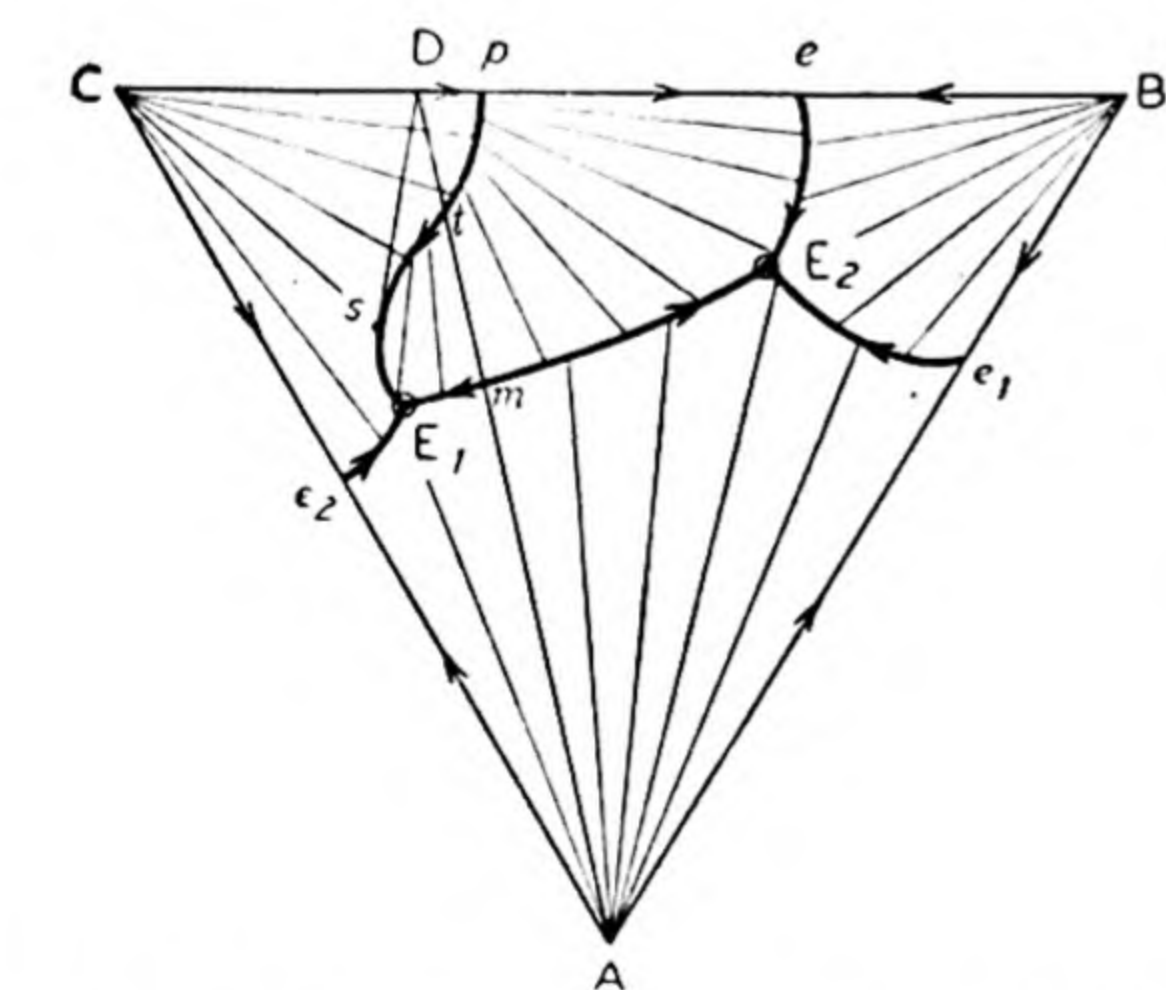


FIG. 12-36. Variation of Fig. 12-34.

tangent to the curve, and becomes one of even reaction ($C +, D +$) from s to the eutectic E_1 . With the exception of the region Dtp , the rest of the triangle DBA behaves in the ordinary eutectic fashion, with respect

to the solids D, B, and A. For the triangle CDA, compositions in the region ACstA (*st* being the curve), also behave in simple eutectic fashion, with respect to C, D, and A. Compositions in CstD precipitate C and reach the curve *ps*. For those in CDs, the solid C is dissolved at the expense of D as the liquid travels toward *s*, but beyond this point C is precipitated together with D, as the liquid proceeds to E_1 . For those in *sDt*, the solid changes completely to D while the liquid is on the section *ts* of the curve, whereupon it crosses the curve into the D field to reach either sE_1 or E_1m , and finally the ternary eutectic E_1 . For this region, then, (*sDt*), the primary

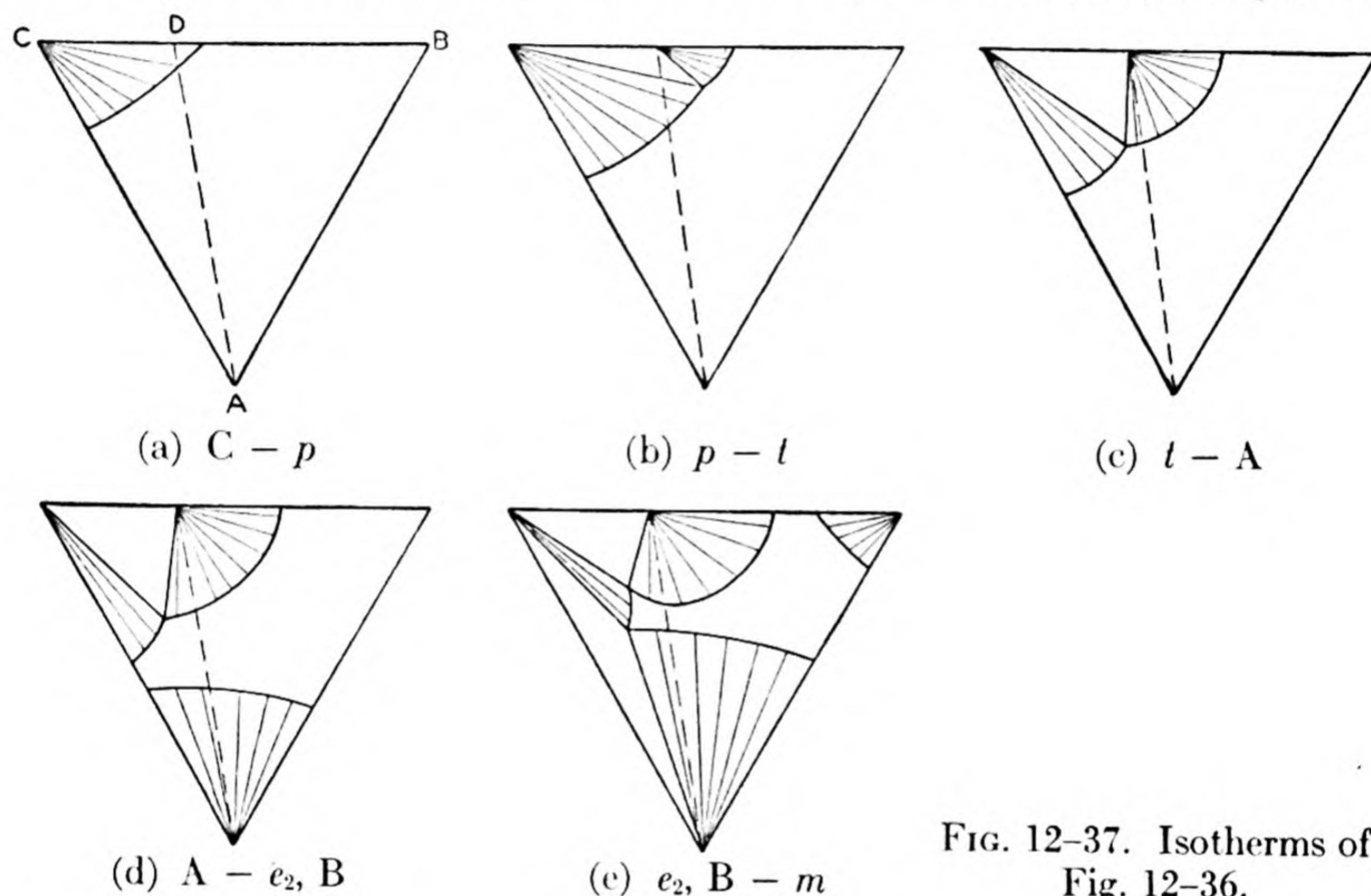


FIG. 12-37. Isotherms of Fig. 12-36.

crystallization product changes from C to D, and C reappears either as a second product, for the liquids originally on the left of the line DE_1 , or, finally, for the others, as a third product, at the eutectic E_1 itself.

If the primary product C is “effectively removed” during crystallization, that is, if it is not given time to redissolve when the liquid reaches the curve pE_1 , then those liquids in the section below the line *Ct* reach E_1 as a crystallization end-point while those above this line reach E_2 . In Fig. 12-34 such non-equilibrium crystallization leads to E for all ternary compositions.

Some isotherms for the system of Fig. 12-36 are shown in Fig. 12-37; they may be considered followed by Figs. 12-29(g-i). Although point *m* of Fig. 12-36 is a “saddle point” on the eutectic curve E_1E_2 , the vertical section DA is not quasi-binary.

If B is water, and C and A are two salts (with common ion), then D is a hydrate of C. In Fig. 12-35(a), at $T > p$, D is metastable with respect to C;

in 12-35(d), at $T < P$, C, the anhydrous salt, is metastable with respect to D, the hydrate. Hence, as seen in Fig. 12-38, the metastable solubility curve of the hydrate lies below that of the anhydrous salt, at the temperature

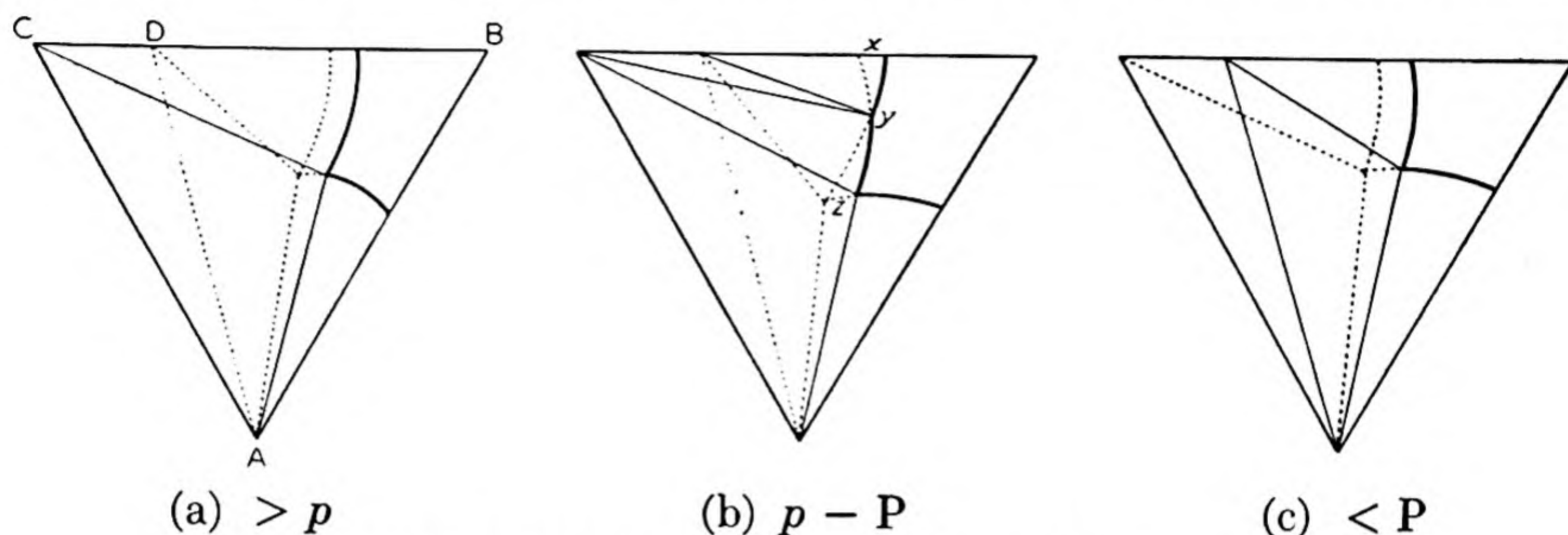


FIG. 12-38. Stable and metastable solubility curves.

above the binary peritectic or transition point p , while the metastable solubility of the anhydrous salt is greater than that of the hydrate at a temperature below the ternary peritectic or transition point P . In the range between p and P (Fig. 12-38(b)) the two solubility curves cross each other at a point y , and the hydrate is stable, (section xy) in low concentrations of A, while the anhydrous salt is the stable saturating phase in high concentrations of A (section yz).

In terms of the activity or vapor pressure of B (water), the component A, at the temperature of the isotherm, lowers the vapor pressure of the water from the solution saturated with the hydrate D, until, at the point y , the hydrate is no longer stable and is dehydrated to C. If the isotherm refers to a condensed system of two non-volatile substances and water (B), the vapor pressure of the solution y is that of the *binary* equilibrium $C + D$ (hydrate) + vapor (B, H_2O) at the same temperature and under the same (atmospheric) pressure.

Some of the foregoing relations may be illustrated with the system KCl (A)–NaCl (B)– $CdCl_2$ (C), shown in Fig. 12-39,⁹ involving three binary compounds, one with congruent melting point ($D_2 = CdCl_2 \cdot KCl$) and two incongruently melting compounds ($D_1 = CdCl_2 \cdot 4KCl$ and $D_3 = CdCl_2 \cdot 2NaCl$). The latter illustrates Fig. 12-36, since the two-fold saturation curve entering the diagram at the binary peritectic p_3 starts as a transition curve, with the odd reaction $B - , D_3 +$, and becomes a curve of even reaction, to end at a ternary eutectic, E_2 . The crystallization fields for A(KCl) and B(NaCl) are continuous around the point K. The curve KP corresponds to KE of Fig. 12-13. The binary system

⁹ I. C. T., IV-75, 80.

KCl–NaCl forms a continuous solid solution with a minimum melting point (point m). At about 405° this solid solution begins to split, the point K being at the temperature of the upper critical solution point. The miscibility gap widens as T falls, and we are assuming that the salts A and B appear as pure solids at the temperature of the invariant P . The crystallization paths in the general field Ap_1Pp_3B are therefore represented as curved as long as T is $>P$. The other four solids are pure and hence the paths in these four fields are straight lines. There are three ternary eutectics, E_1 , E_2 , and E_3 , congruent solidification end-points for the triangles

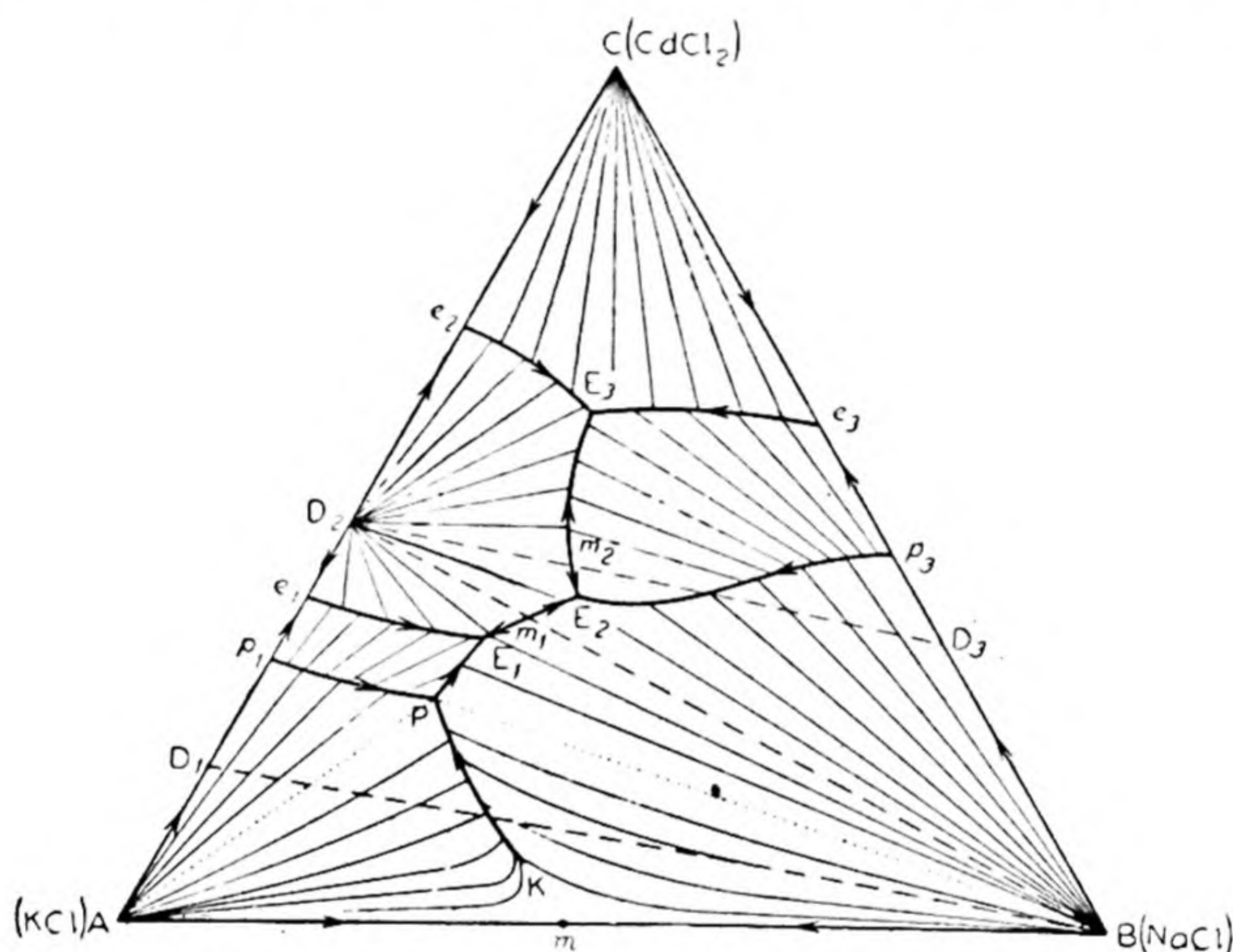


FIG. 12-39. System KCl–NaCl–CdCl₂.

D_1D_2B , D_2D_3B , and CD_2D_3 respectively. Points m_1 and m_2 are saddle points, but only the section D_2B is quasi-binary, since D_3 is incongruently melting. P is a ternary transition or peritectic point, type B , for the reaction $A + L \rightarrow D_1 + B + \text{cals.}$; it is reached by all liquids with compositions in the quadrangle AD_1PB . Those originating in D_1PB lose solid KCl at the invariant P and proceed to the eutectic E_1 for final solidification. Compositions in the triangle AD_1B , on the other hand, solidify completely with P as their incongruent crystallization end-point. The final solids in this triangle (AD_1B) include pure KCl and pure NaCl if the binary solid solubility has diminished to zero at P .

3. Compound with Inverse Peritectic

The field for a compound like D_5 of Fig. 12-23, with a lower transition point at which it decomposes into $C + L$, at the pressure of the ternary T/c prism, is one which merely interrupts that of the component C on the

CB border, as in Fig. 12-40, for an incongruently melting compound. The points p and p' are the upper and lower transition points (the equilibria $D \rightleftharpoons C + L$) of the compound. The D field is closed entirely within the C field by a continuous curve pp' , since the only possible three-solid equilibrium is one involving $A + B + C$ (the eutectic E). The lines Ds and Cs' are tangents to the curve pp' , which is odd in reaction from p to s ($C-$, $D+$), even, between s and s' ($C+$, $D+$) and odd again from s' to p' ($C+$, $D-$). Liquids in Cps' reach ps' with primary crystallization of C. If the

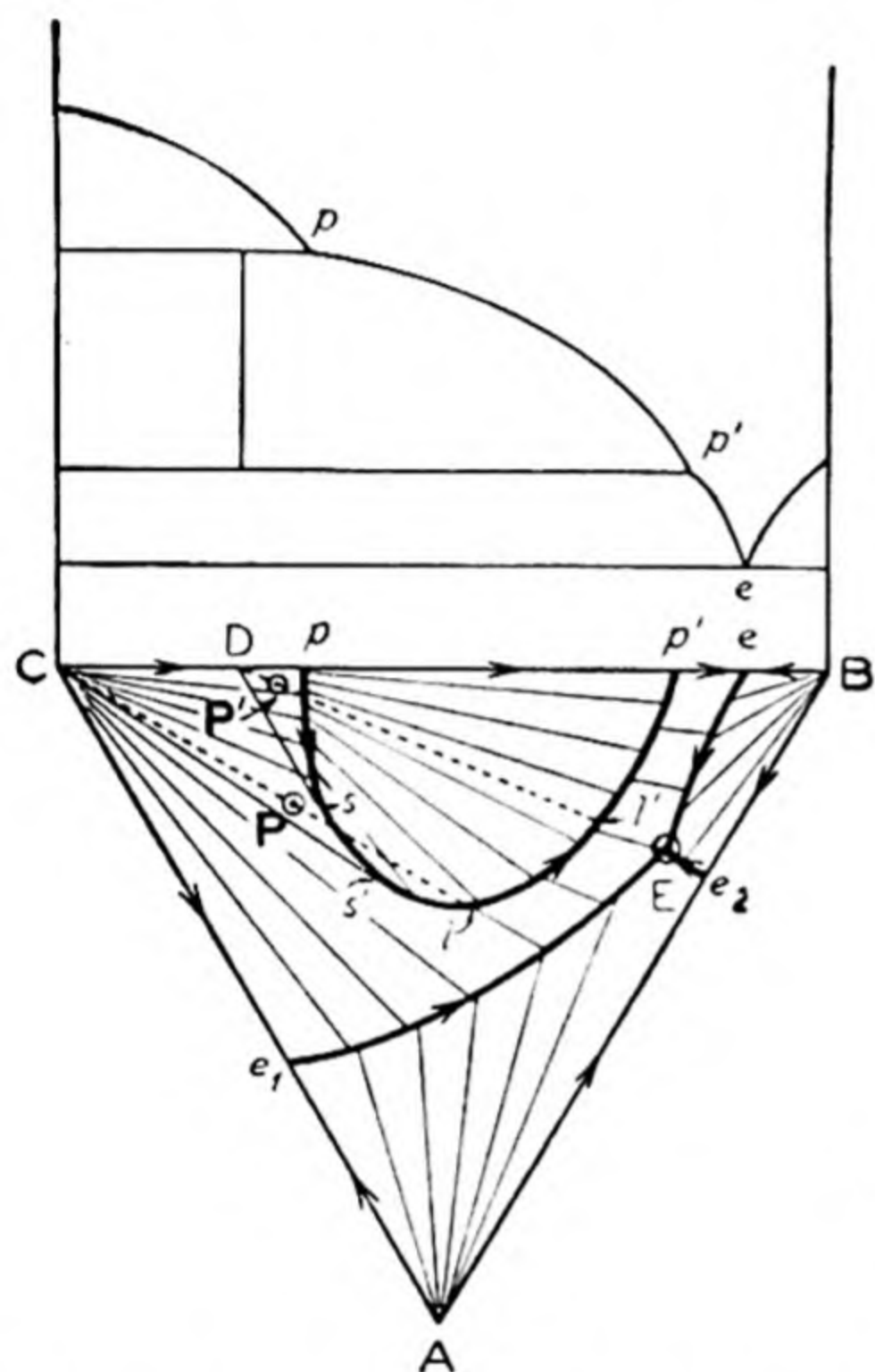


FIG. 12-40. Incongruently melting binary compound with inverse fusion point.

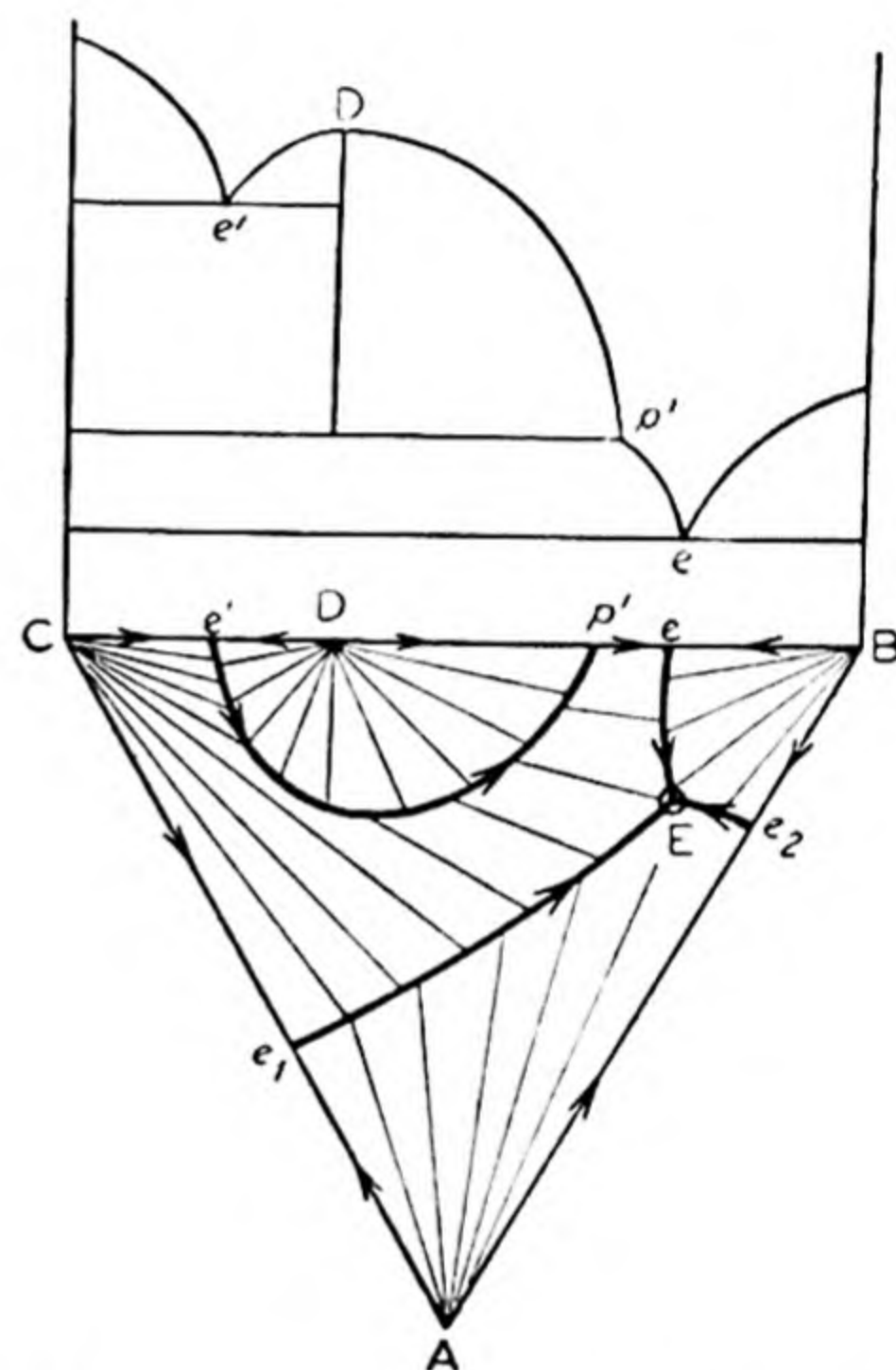


FIG. 12-41. Congruently melting binary compound with inverse fusion point.

original composition is P (other than in Dps) then the quantity of D formed as the liquid travels on the curve first increases and then decreases, vanishing when the liquid reaches point l . Here the liquid, saturated again with C alone, enters the C field to proceed to one of the eutectic curves and finally to E. If the composition is P' , in Dps , solid C is all consumed while the liquid travels on the curve toward s , and, before it reaches s , it enters the D field and crosses it on a crystallization path away from D. When it again meets the curve, as at point l' , and travels toward p' , C begins to precipitate again and eventually D disappears, to leave $L + C$, L being on the curve $s'p'$ and on the straight line CP' .

If D is congruently melting but with an inverse peritectic, as in Fig. 12-41, then the ternary relations are essentially the same as those of Fig. 12-40, except that D is a maximum point on the boundary of the D field, while point p becomes the eutectic e' , between C and D.

4. Compound Decomposing into Two Solids

The case of type D_3 of Fig. 12-23, a compound stable at the binary melting point relations but decomposing into two different solids above the ternary eutectic, is shown in Figs. 12-42 and 12-43. In Fig. 12-42, the binary compound is incongruently melting, whereas in 12-43, congruently melting. In either case the two boundaries of the D field originating at the CB side meet at the point P, which is at the decomposition temperature T_P of the binary system (at the specified pressure) for the reaction $D \rightarrow C + B + \text{cals.}$ The invariant reaction at point P is the same, $D \rightarrow C + B + \text{cals.}$, but in the presence of the liquid phase (P) containing A. During this reaction the liquid (P) remains constant both in composition and in actual quantity, since the component A is present only in this invariant liquid phase and does not take part in the phase reaction involved,

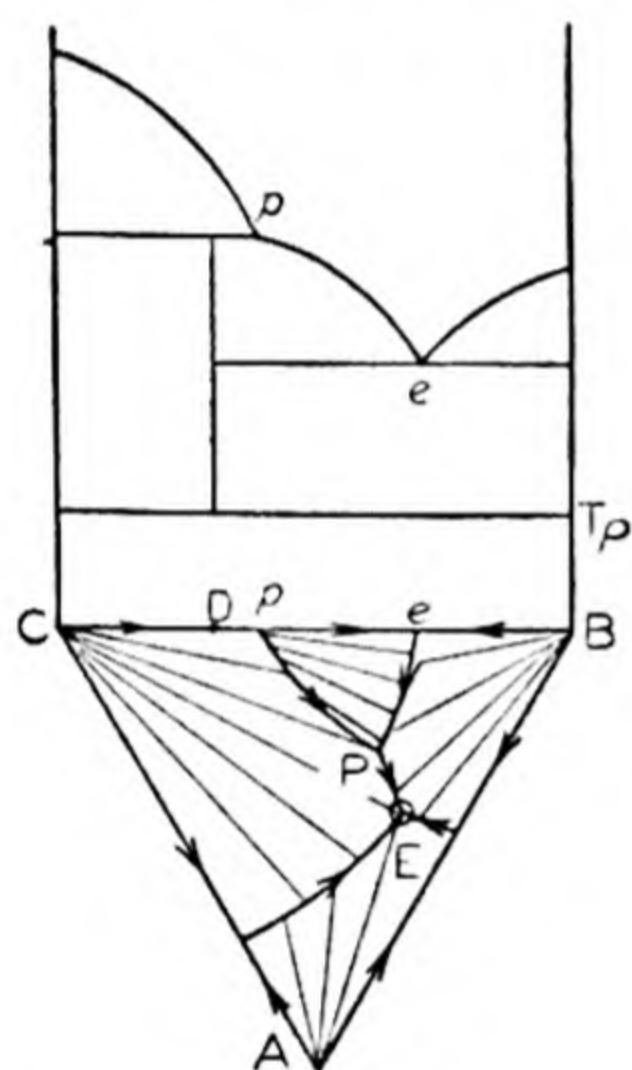


FIG. 12-42. Incongruently melting binary compound decomposing above ternary eutectic.

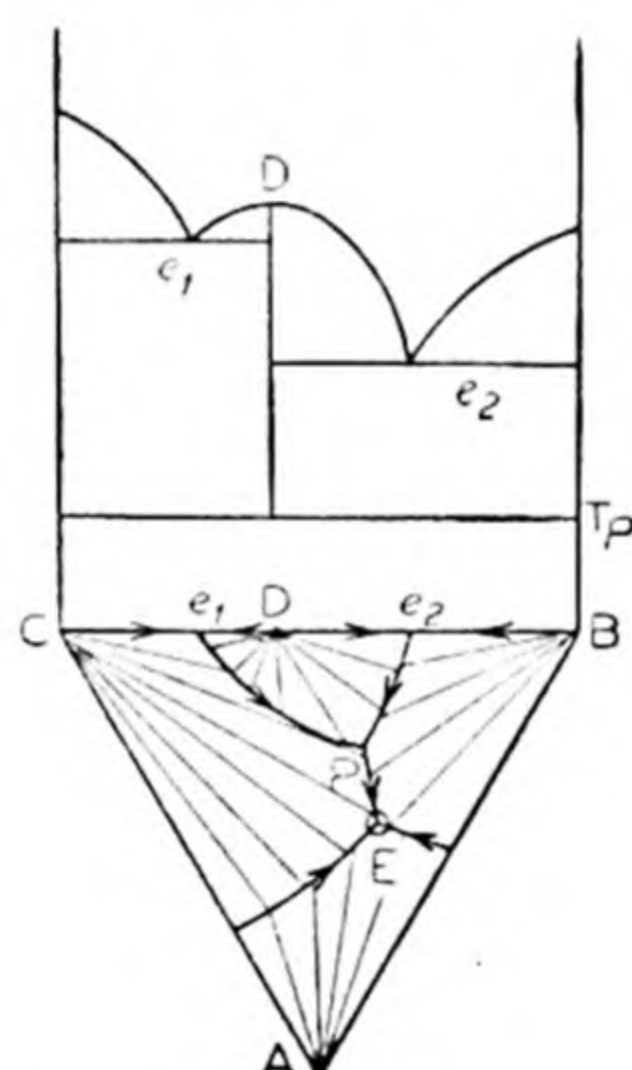


FIG. 12-43. Congruently melting binary compound decomposing above ternary eutectic.

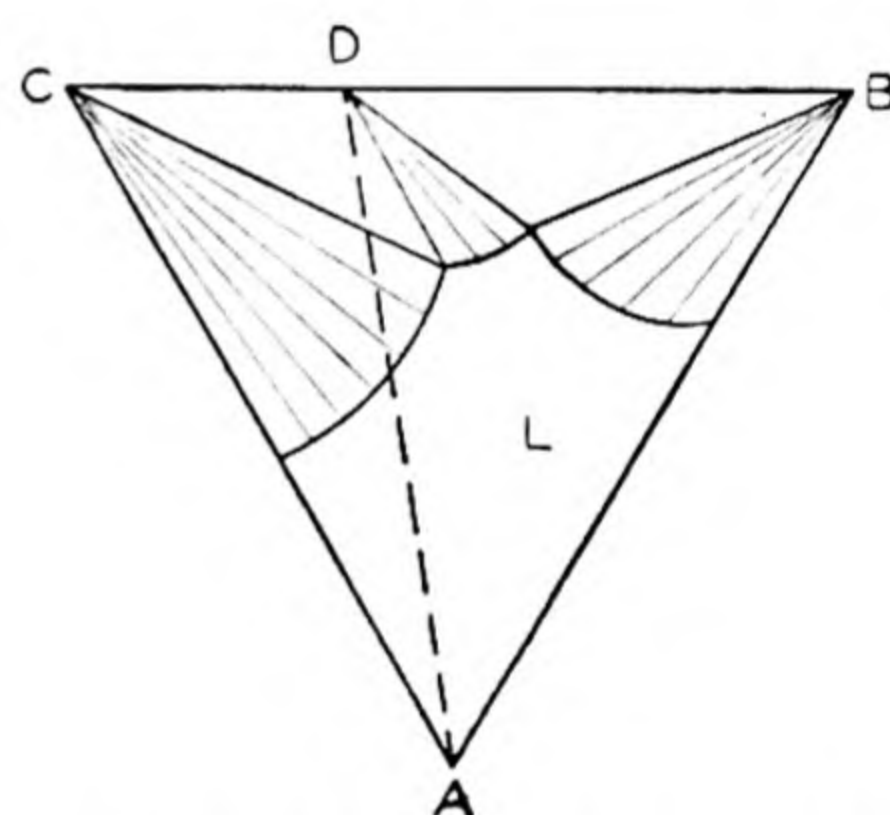


FIG. 12-44. Isotherm of Fig. 12-42, between e and P.

which is strictly binary, an equilibrium of lower order. This point is therefore never even an incongruent crystallization end-point since its solid phases do not include the component A, and all ternary compositions must solidify to $A + B + C$. Fig. 12-44 is an isotherm between e and P for Fig. 12-42; the tie-line area $D + L$, which appeared at the temperature of the peritectic p , vanishes at the temperature P. Fig. 12-43 may be taken as schematic for the relations in the system KCl (A)–KF (B)– CaF_2 (C), with the binary compound $\text{KF} \cdot \text{CaF}_2$.¹⁰

A compound of the type D_1 of Fig. 12-23, or, more simply, that of Fig. 12-45(a), may appear with falling T , as a stable saturating solid phase in

¹⁰ I. E. Krause and A. G. Bergmann, *Compt. rend. acad. sci. U.R.S.S.* 35, 20 (1942).

the ternary system, at the decomposition temperature T_P , for the reaction $D \rightleftharpoons C + B - \text{cals.}$, at the pressure of the prism. Its field will lie entirely within the ABC composition plane, since the compound cannot saturate stably any binary solution. The field appears, therefore, at point P on the

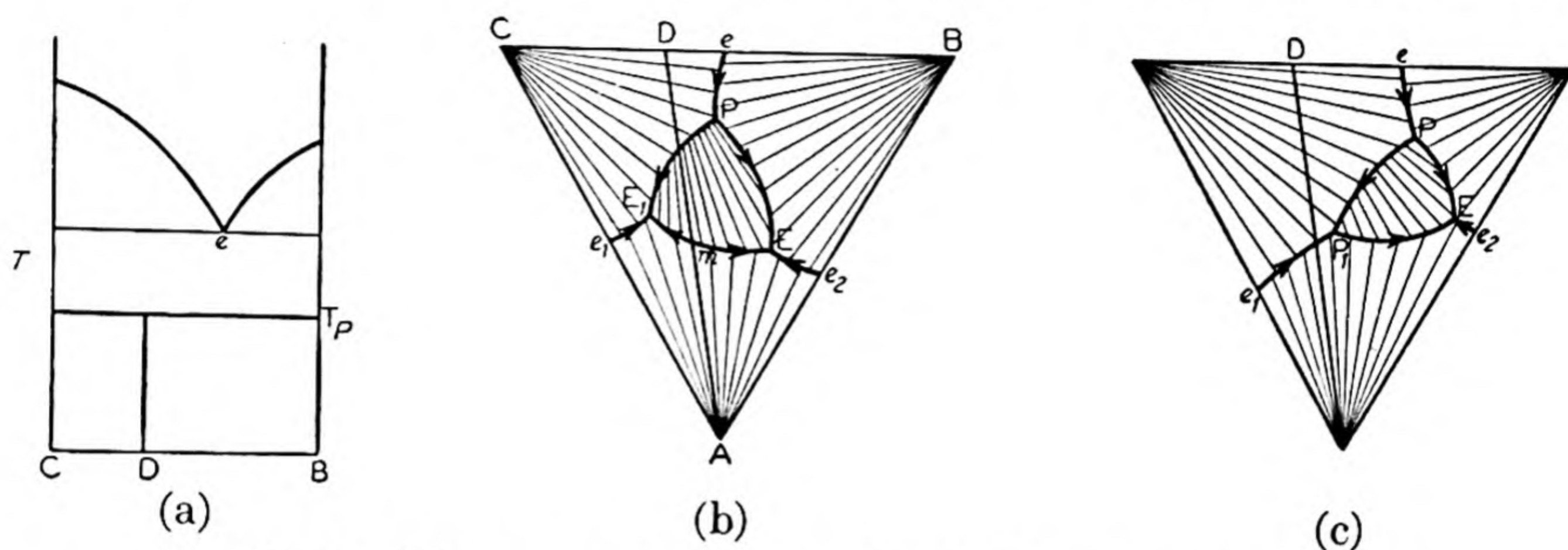


FIG. 12-45. Binary compound unstable in binary liquid system.

curve eP from the CB eutectic at the temperature T_P of Fig. 12-45(a); the invariant reaction at P is $C + B \rightarrow D + \text{cals.}$, in presence of a liquid containing A. Again the liquid P is constant both in composition and in actual quantity during the invariant phase reaction, just as in the case of Figs. 12-42 and 12-43. (These relations are illustrated by the binary compound $3\text{CaO} \cdot \text{SiO}_2$ in the ternary system $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$. The invariant point P involves the solids CaO and $2\text{CaO} \cdot \text{SiO}_2$, in the reaction $\text{CaO} + 2\text{CaO} \cdot \text{SiO}_2 \rightarrow 3\text{CaO} \cdot \text{SiO}_2 + \text{cals.}$ in presence of the ternary liquid containing Al_2O_3 in

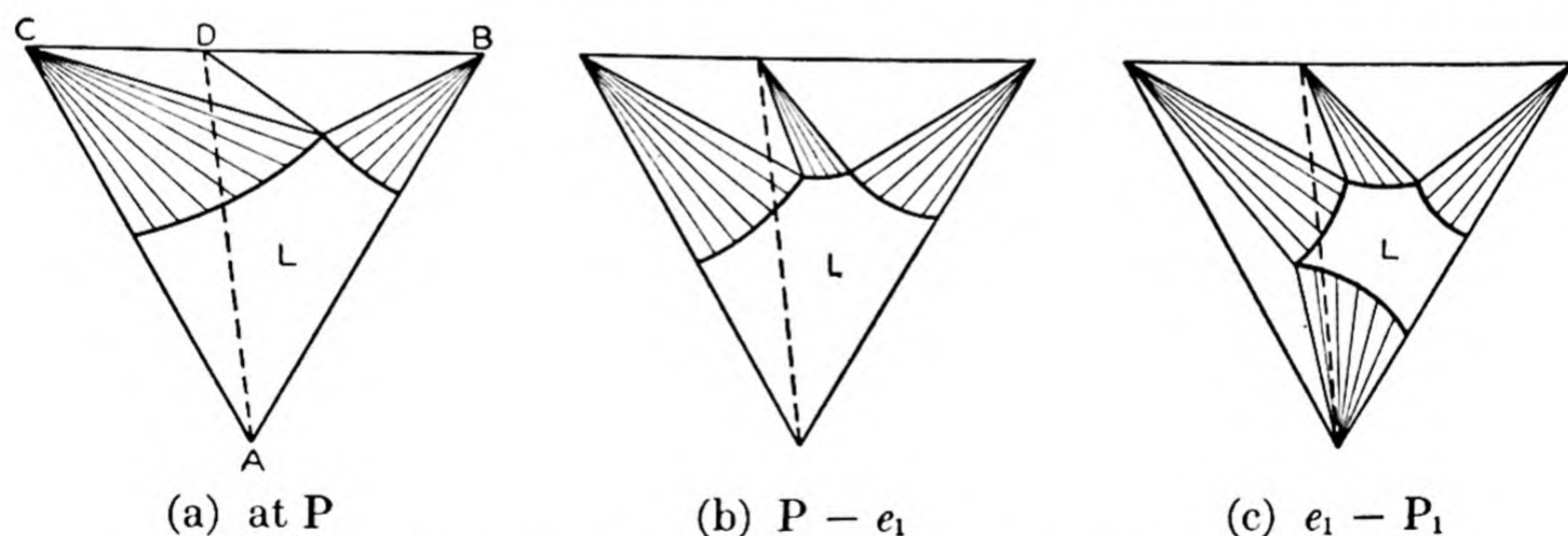


FIG. 12-46. Isotherms of Fig. 12-45(c).

addition, at the temperature 1900° .)¹¹ Two new curves therefore arise at point P, leaving it with falling T , one for the equilibrium LCD, the other for LBD. These will give rise to two ternary invariants; and as discussed under Fig. 12-25, these may be two ternary eutectics (Fig. 12-45(b)), or a peritectic and a eutectic (Fig. 12-45(c)). For temperatures below the point

¹¹ *I. C. T.*, IV-93.

P, therefore, the relations are similar respectively to those of Figs. 12-25(a) and (b). Some isotherms are shown in Fig. 12-46; Fig. 12-46(c) may be considered followed by 12-30(b) and (c). The point P is reached by all compositions in the triangle CBP. Of these, compositions in CDP lose the B phase at P and travel on the curves PE_1 or PP_1 , while those in DPB lose the C phase at P and proceed to the eutectic E to solidify to $A + D + B$. Point P_1 of Fig. 12-45(c) is reached by all compositions in the quadrangle CDP₁A, and with the invariant reaction $L + C \rightarrow D + A + \text{cals.}$, it is the incongruent crystallization end-point for the triangle CDA.

D. Systems with Parallel Binary Compounds (Which May Be Isomorphous)

We shall let A_1 represent a compound of A and C, and B_1 the parallel or corresponding compound of B and C, "parallel" in the sense that the mole fraction of C is the same in both compounds. If C is water, for example, and A and B are salts with common ion, then A_1 and B_1 represent corresponding hydrates of the salts. There will be a great number of different relations in such a system, depending on whether the binary compounds melt congruently or not, and on whether or not solid solutions are formed between the two components A and B and between the two compounds A_1 and B_1 ; the solid C will be assumed to be always pure.

1. The Compounds Both Melt Congruently, and the Section A_1B_1 Is Quasi-binary

In this case, whatever the relations between the compounds, the condensed system A_1 -C- B_1 may be considered as a separate ternary system described by the relations already discussed, and we need consider only the

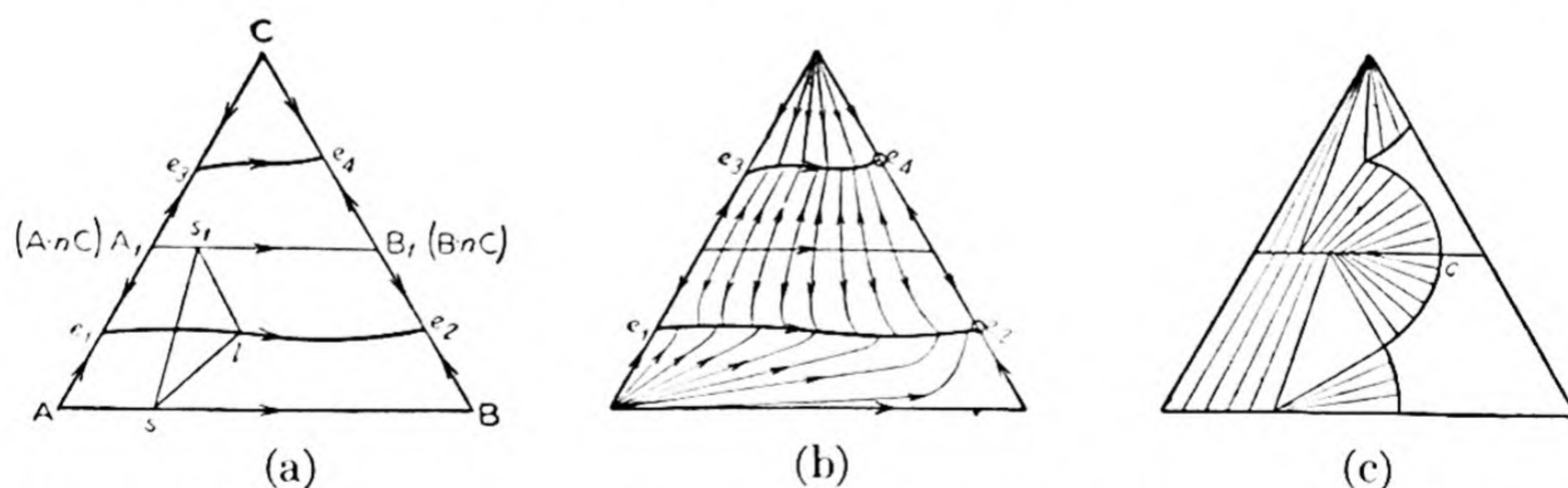
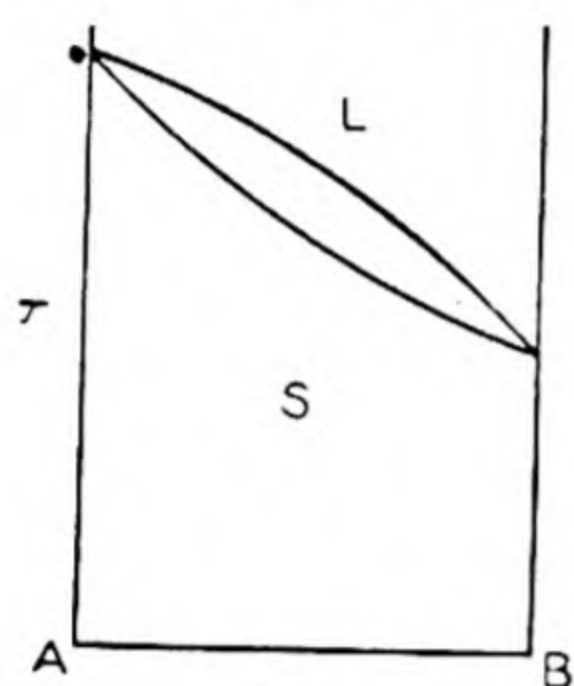


FIG. 12-47. Congruently melting compounds with continuous solid solution.

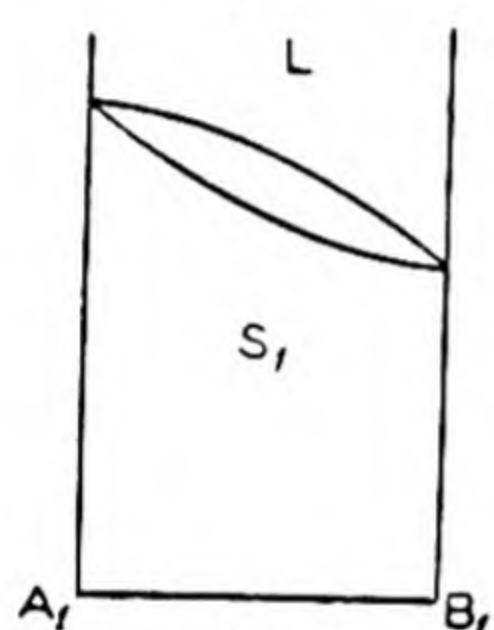
part of the system defined by the trapezoid AA_1B_1B (Fig. 12-47(a)). The line A_1B_1 is parallel to the base if the composition is plotted in moles. The substances Fe-FeS-CdS-Cd or Ba-BaCl₂-MgCl₂-Mg would constitute

such a system, which is merely then a simple displacement system, involving the reaction $A + BC_n \rightleftharpoons AC_n + B$.¹²

a. If there is continuous solid solution both in the system A–B and in the system A_1B_1 , the polytherm may appear as in 12–47(a). The eutectic curve e_1e_2 is liquid saturated with two solid solutions, solid s on the base AB and solid s_1 on the line A_1B_1 ; the curve e_3e_4 is a similar eutectic curve for liquid saturated with pure C and s_1 . If the solid solutions of the two



(a)



(b)

FIG. 12–48. Vertical sections of Fig. 12–47.

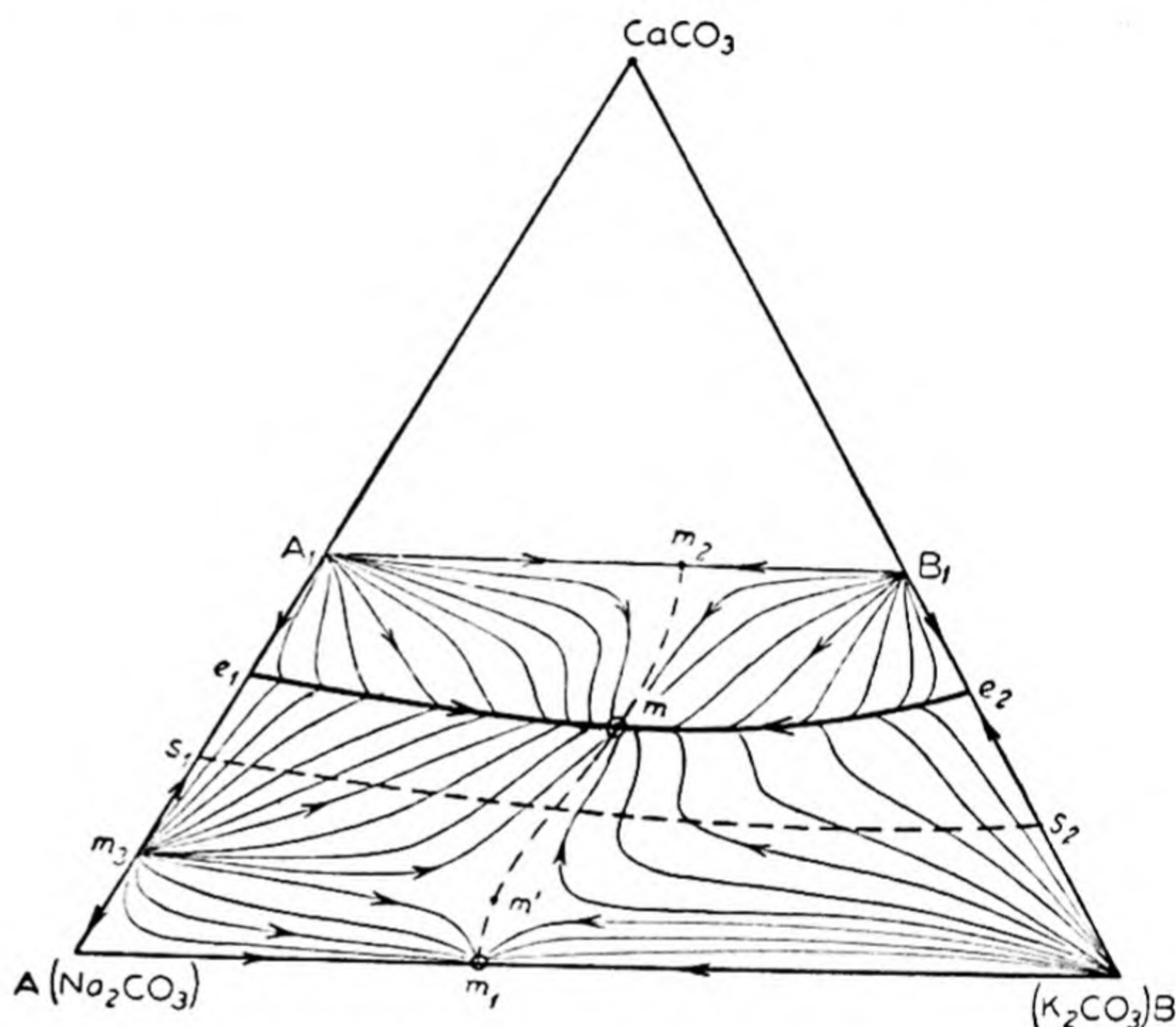


FIG. 12–49. Part of system $\text{Na}_2\text{CO}_3\text{--CaCO}_3\text{--K}_2\text{CO}_3$.

condensed binary systems A–B and A_1B_1 are both assumed simple or “ascendant,” the temperature falls continuously from one side of the figure to the other, on all lines and curves, and vertical T/c sections from A to B and from A_1 to B_1 appear as in Fig. 12–48(a) and (b). The crystallization surface of the A_1B_1 solid solution extends from e_1e_2 to e_3e_4 , with a rounded ridge of maximum temperature represented in projection by the straight line A_1B_1 . Fig 12–47(b) shows the crystallization paths for “effective removal of solid”; only those in the C field are straight. The solidification end-points are e_2 and e_4 . Fig. 12–47(c) is a schematic isotherm below the temperatures e_1 and e_3 but above the melting points of B_1 and B. As T falls further the point c moves to the right on the line A_1B_1 and comes to touch B_1 at the congruent melting point of that binary compound.

Variations are, of course, possible, with maxima or minima of T , in both the AB and the A_1B_1 solid solutions, and correspondingly on the eutectic

¹² For an example of this type of system with a 2-liquid binodal curve, see the diagram for Fe–FeS–MnS–Mn in R. Vogel (Ref. V), p. 342.

curves; in such cases there will be a point of contact of the liquid and solid curves in the T/c sections.

Fig. 12-49 is a schematic polythermal projection of the liquidus of the system Na_2CO_3 (A)– $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3$ (A_1)– $\text{K}_2\text{CO}_3 \cdot \text{CaCO}_3$ (B_1)– K_2CO_3 (B), or part of the system Na_2CO_3 (A)– CaCO_3 (C)– K_2CO_3 (B), studied at a pressure of 1 atm of CO_2 .¹³ The two double salts form a continuous solid solution with a minimum at m_2 ; the two simple salts also form a continuous solid solution which has a minimum at m_1 and which in addition dissolves some CaCO_3 , so that it is actually ternary, with a limit on the curve s_1s_2 . The eutectic curve e_1e_2 , with a minimum at m , represents solution saturated with one solid solution on the line A_1B_1 and one on the curve s_1s_2 . Point m_3 is a maximum on the binary side AA_1 and there is consequently a saddle point at m' . The thin lines on the figure are the schematic crystallization paths, the crystallization end-points being m and m_1 .

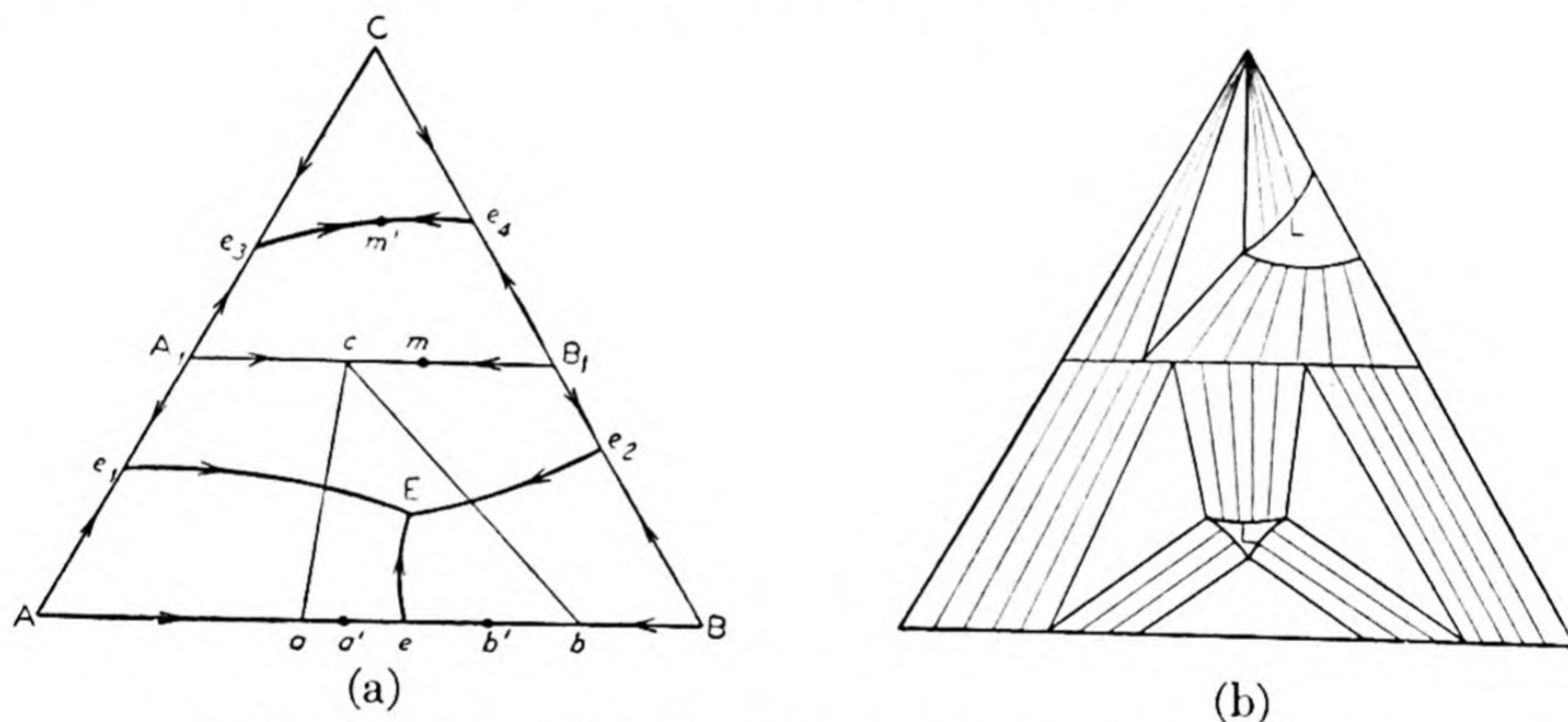


FIG. 12-50. MG in the AB solid solution (eutectic).

b. If one of the solid solutions is discontinuous at the temperature of the eutectic e_1e_2 , a 3-solid invariant appears in the ternary trapezoid. The example in Fig. 12-50 involves a minimum m on the A_1B_1 solid solution (also m' on e_3e_4), a eutectic break, e , in the binary A – B system, and a consequent ternary eutectic E . The A – B miscibility gap is assumed to widen from $a'b'$ at the temperature of e to ab at E . At E ternary liquid is in equilibrium with the conjugate solid solutions a and b , and with a solid solution c which may be on either side of m on the line A_1B_1 . Liquids with original compositions in the region AA_1ca solidify on the curve e_1E to a mixture of s (on Aa') and s_1 (on A_1c), before reaching E ; those in BB_1cb similarly solidify on e_2E to $s + s_1$, without reaching E . The eutectic E is reached only by liquids originally in the eutectic triangle acb , along e_1E

¹³ P. Niggli, *Z. anorg. Chem.*, **106**, 126 (1919).

carrying s_1 and A-rich s , along e_2E carrying s_1 and B-rich s , and along eE carrying conjugate solid solutions of $A + B$, one on each side of the gap $a'b'$. Fig. 12-50(b) is an isotherm slightly above E and between e_3 and e_4 .

In Fig. 12-51 there is a eutectic e in the binary A_1B_1 system (and only a

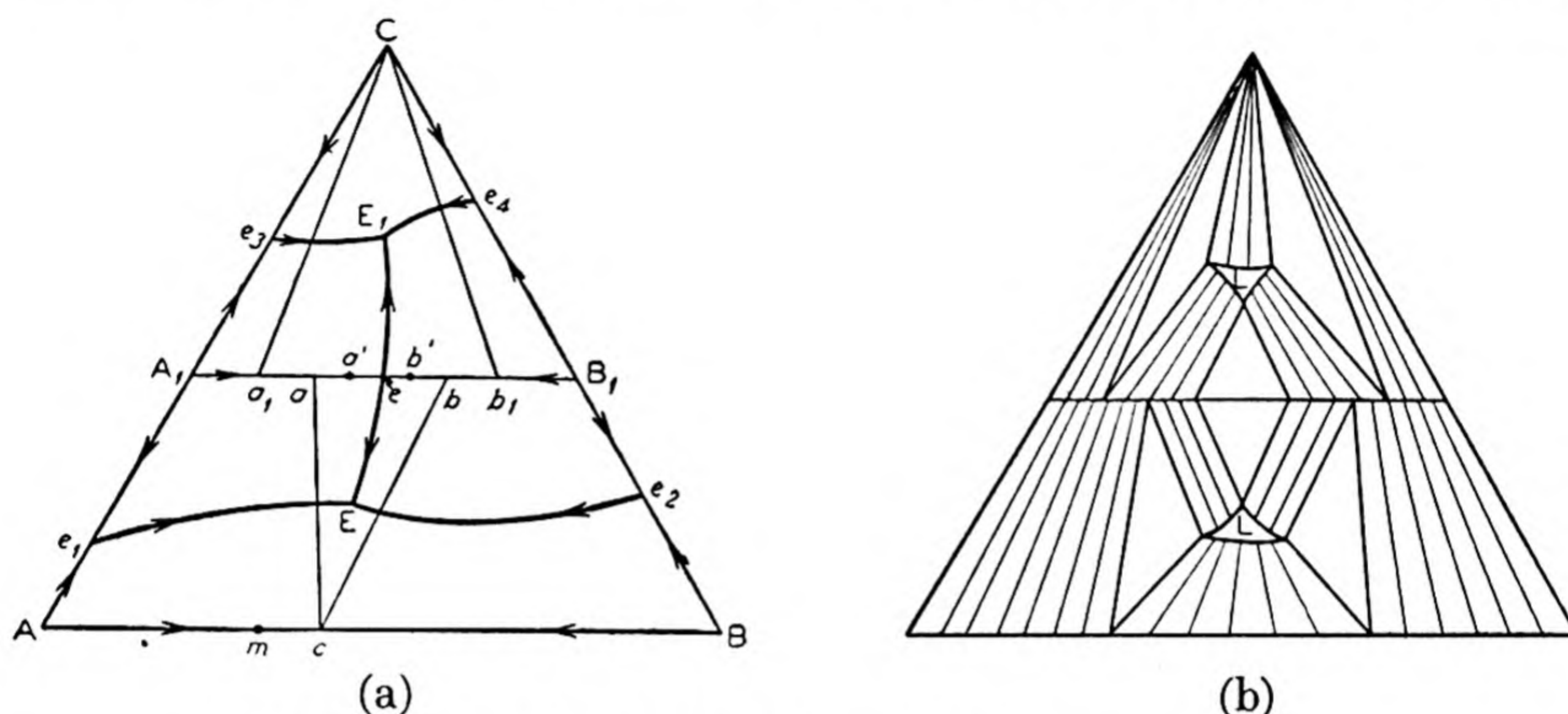


FIG. 12-51. MG in the A_1B_1 solid solution (eutectic).

minimum m in the $A-B$ system), with two consequent ternary eutectics: E in the trapezoid, for $L +$ the three solid solutions c , a , and b ; and E_1 (at a temperature here assumed lower than E) in the upper triangle, for $L + C +$ the two solid solutions a_1 and b_1 . The MG in A_1B_1 widens from $a'b'$ at e to ab at E , and to a_1b_1 at E_1 . Point e is now a saddle point of maximum T on curve EE_1 for liquid saturated with conjugate solid solutions on the line A_1B_1 . The relations at E are entirely similar to those already discussed for Fig. 12-50, and those at E_1 are as in Fig. 12-9. Fig. 12-51(b) is an isotherm between e and the two ternary eutectics and below e_1-e_4 .

In Fig. 12-52 there is a peritectic break p in the $A-B$ system. The $A-B$ miscibility gap widens from $a'b'$ at p to ab at the ternary peritectic P . Liquids with original composition in AA_1ca solidify on curve e_1P to a mixture $s + s_1$ without reaching P . Point P is reached only by liquids falling in the invariant quadrangle $acPb$, along e_1P carrying $s + s_1$, and along pP carrying A-rich s and B-rich s as conjugate solid solutions. The diagonal invariant reaction at P is $L + a \rightarrow c + b$, so that P is the incongruent solidification end-point for triangle acb . Compositions in the triangle cbP lose the a phase at the invariant and travel along Pe_2 to solidify as $s + s_1$. Liquids originating in the region bPp reach the curve pP , along which the reaction is odd, A-rich s dissolving at the expense of B-rich s ; such liquids leave the peritectic curve pP before reaching P , and travel across the field pPe_2B to the eutectic curve Pe_2 , along which they solidify, before reaching e_2 , to leave a mixture of s on bB , and s_1 on cB_1 .

c. Finally, we shall assume no solid solution in either of the systems A-B and A₁-B₁. Complete solidification now leads to one of the two possible arrangements discussed under Fig. 12-32(a, b), in connection with Guertler's *Klärkreuzverfahren*. In one arrangement (Fig. 12-53), the pair of solid phases A + BC (that is, B₁) may coexist at equilibrium while the pair AC(or A₁) + B cannot; and they may therefore be distinguished as the *stable* and the *unstable pair* respectively. On complete solidification the only 3-solid equilibria possible are A + BC + B and A + BC + AC. In whatever proportions we mix B and AC, at the pressure of the $(T/c)_P$ projection of Fig. 12-53, they react by displacement to give A + BC, leaving either B or AC in excess.

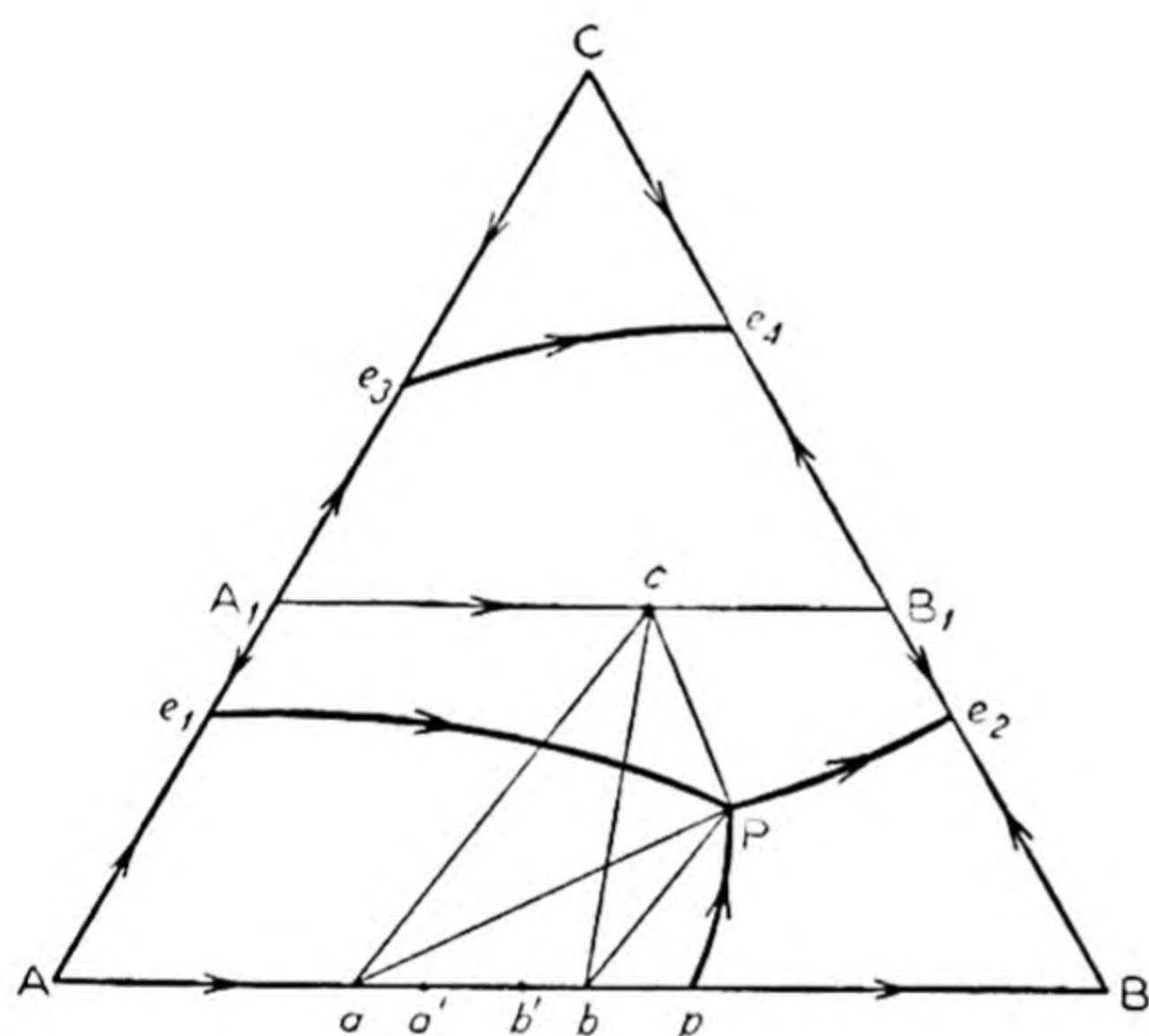


FIG. 12-52. *MG* in the AB solid solution (peritectic).

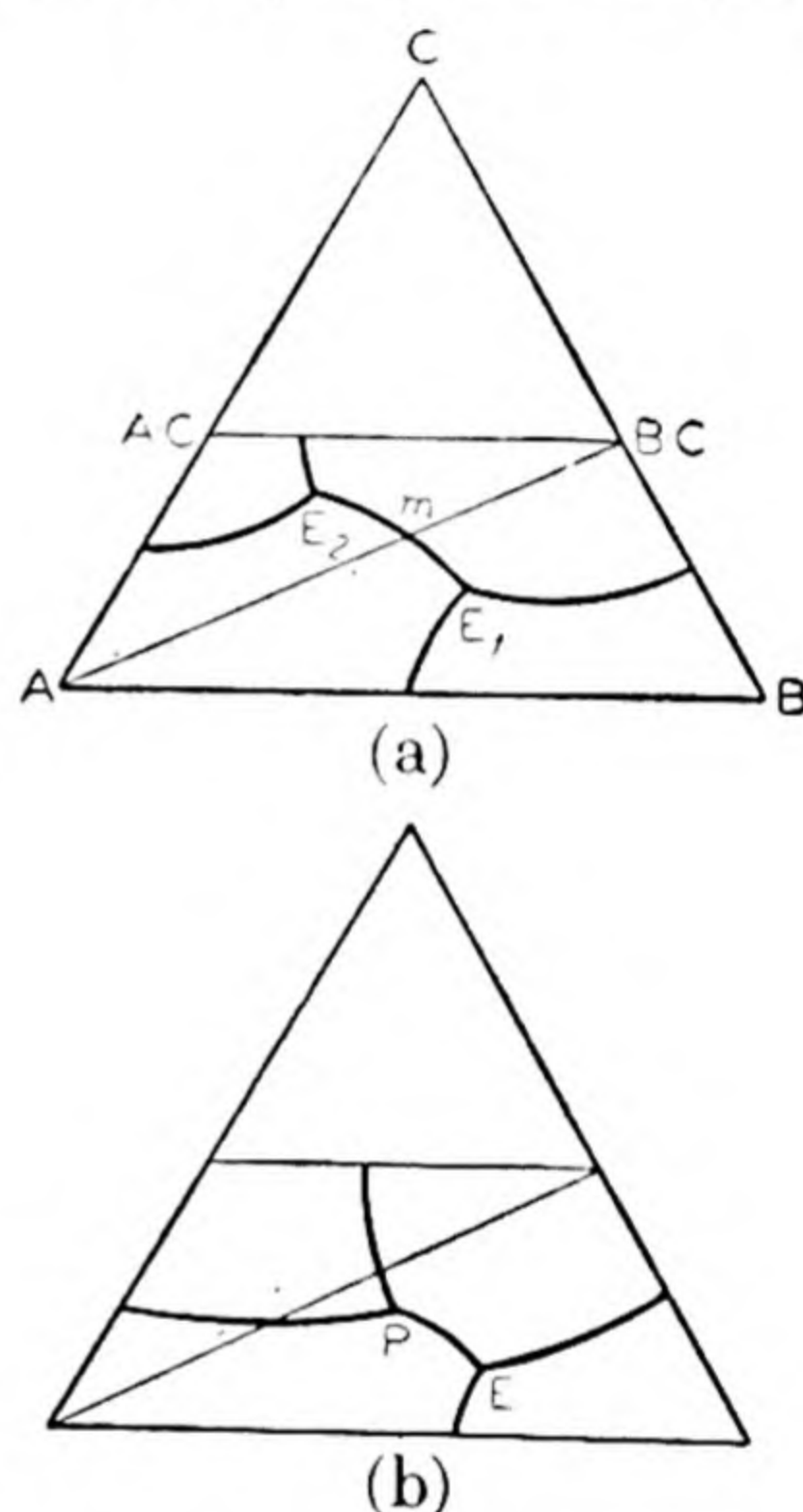


FIG. 12-53. Four solids involved in the trapezoid.

The two invariants for solidification (quadruple points for L + three solids) may be both eutectics, as in 12-53(a), or one peritectic and one eutectic, as in 12-53(b). In either case the curve joining these invariants represents liquid saturated with the stable pair, or A + BC, and there is no equilibrium liquid saturated with the unstable pair, AC + B. In 12-53(a) the line A-BC represents a quasi-binary condensed section, with a saddle point at *m*; in the trapezoid of 12-53(b) there is no quasi-binary section, the temperature falling from P to E. Point P is the incongruent solidification end-point for the triangle A-AC-BC.

With change in pressure, it is conceivable that the stability relations may change, B + AC becoming the stable pair for the melting point equilibrium. The inversion of stability would occur at a quintuple point involving the phases L + A + BC + B + AC. This type of transition

will be discussed further in section F of Chapter XV, especially under Fig. 15-23. In the absence of the liquid phase, or below the melting points, the inversion of stability would occur at a univariant (isothermally or isobarically invariant) 4-phase point of the type called Q_B , discussed in Chapter X, Fig. 10-24.

2. The Compounds Melt Incongruently (Transitions of Hydrated Solid Solutions)

We shall consider now the special case in which A_1 and B_1 are incongruently melting, corresponding hydrates in a ternary aqueous salt system. With all solids assumed pure (no solid solution for any combination) the system appears as in Fig. 12-54(a), with one ternary eutectic and two ternary peritectics. P_1 , with the invariant reaction $L + A \rightarrow A_1 + B + \text{cals.}$,

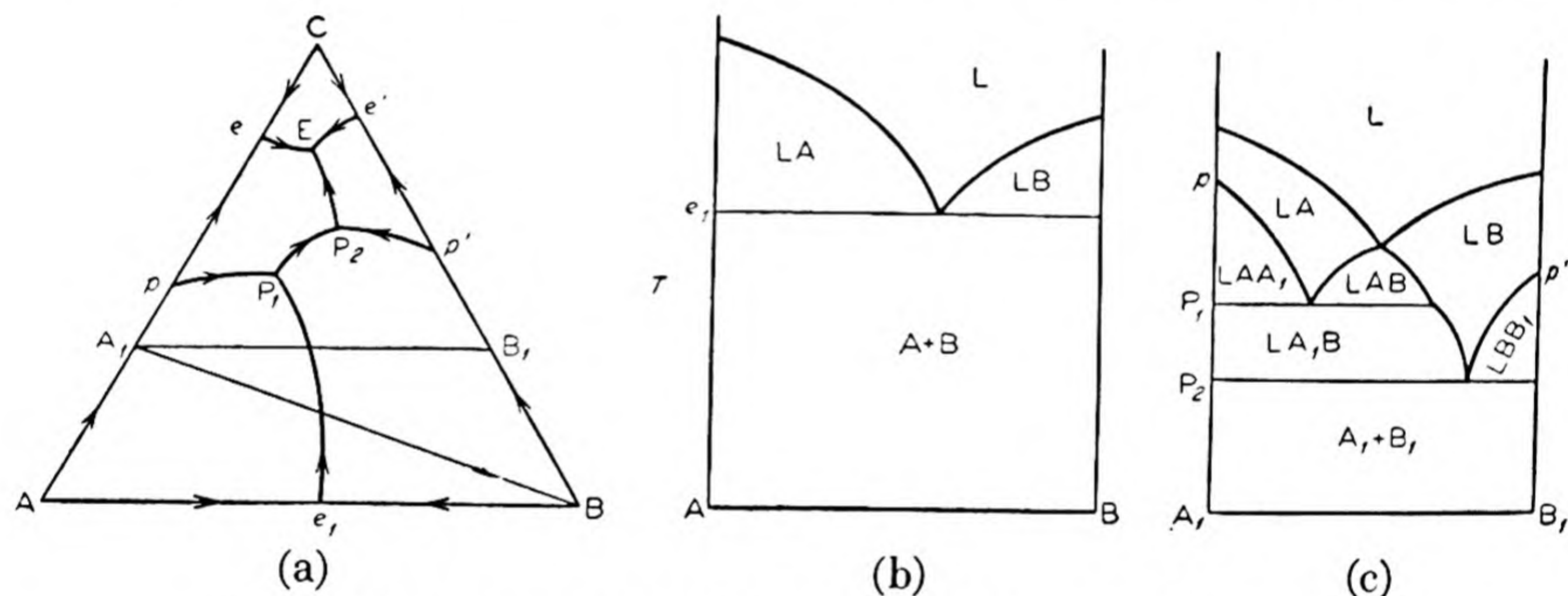


FIG. 12-54. Corresponding hydrates with no solid solution.

is the incongruent crystallization end-point for compositions in the triangle AA_1B . P_2 , with the invariant reaction $L + B \rightarrow A_1 + B_1 + \text{cals.}$, is the incongruent crystallization end-point for the triangle A_1B_1B . Compositions in A_1CB_1 solidify completely at the eutectic E to a mixture of C (ice) and the two hydrates, $A_1 + B_1$. Figs. 12-54(b) and (c) represent vertical, T/c , sections: (b), the binary section AB , and (c), the ternary section through the hydrates, A_1B_1 . The latter will be clear in conjunction with the isotherms of Fig. 12-55. Between 12-55(c) and 12-55(d) the tie-line region $A + L$ vanishes to a single line, at the invariant P_1 , to be replaced by the diagonal A_1B , shown in 12-55(d). The $B + L$ field similarly vanishes at P_2 , to be replaced by the A_1B_1 diagonal of Fig. 12-55(e).

a. If there is continuous solid solution both between the anhydrous salts, A and B , and between the hydrates, A_1 and B_1 , there are only three possible solid phases in the system, which may then appear as in Fig. 12-56 (cf. Fig. 12-47(a)). Some isotherms are shown in Fig. 12-57. In Fig. 12-57(a),

which is above the continuous transition or peritectic curve pp' of Fig. 12-56(a), the solubility curve is that of a continuous solid solution of the anhydrous salts. In 12-57(b) this curve, now lb , crosses that (al) for the solid solution of the hydrates. The tie-lines from the liquid lb therefore run

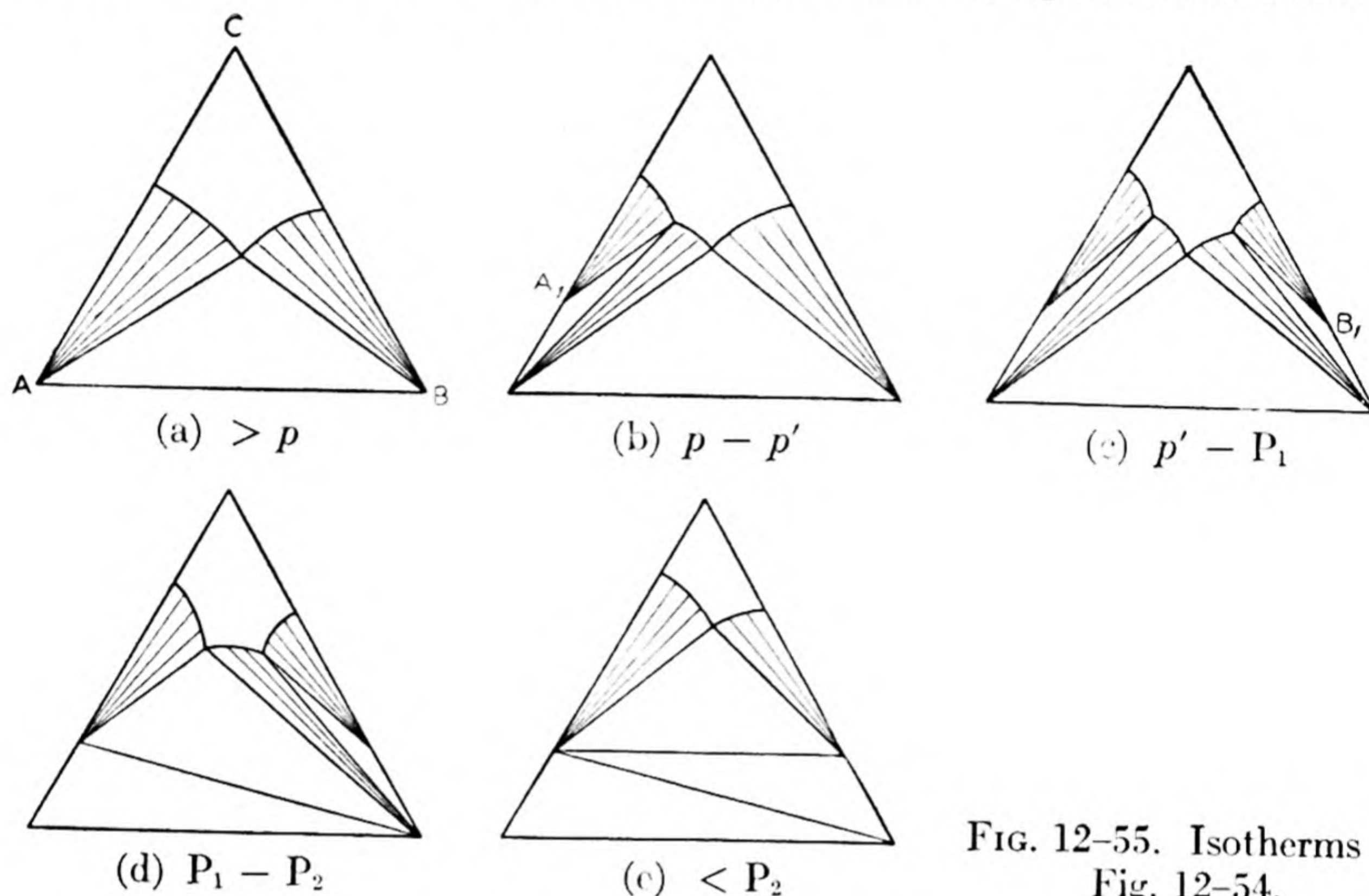


FIG. 12-55. Isotherms of Fig. 12-54.

to the base of the triangle while those for al run to the line connecting A_1 with B_1 ; and the 3-phase triangle ls_1s is isothermally invariant, the liquid being saturated with two solid solutions, an anhydrous one of composition s and a hydrated one of composition s_1 . Solution l is a point on the curve pp'

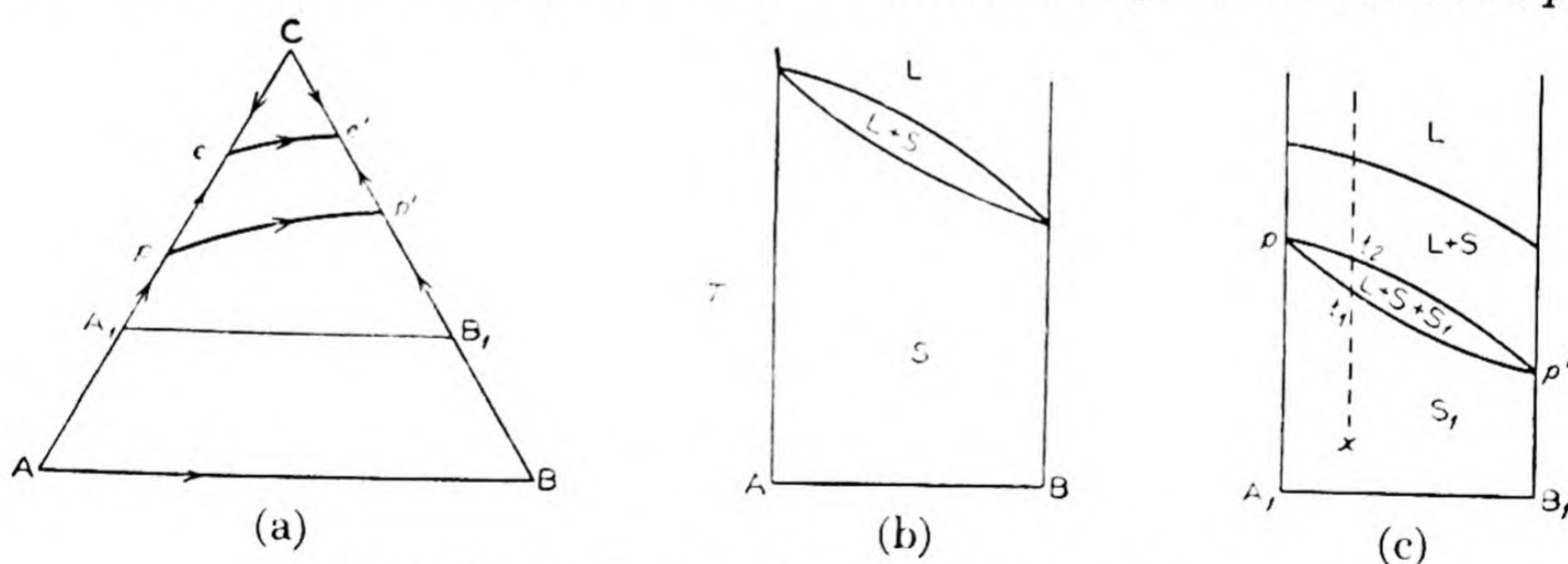


FIG. 12-56. Two continuous solid solutions.

of Fig. 12-56(a). The region between the lines A_1s_1 and As is a 2-phase mixture of solid solutions, one hydrated, the other anhydrous. The tie-lines in this region are not determined when the "solubility isotherm" is studied, which deals only with the curve alb and its tie-lines. In this case, then, the

limit s_1 of the hydrated solid solution does not indicate limited solid solubility, but merely a corner of the invariant 3-phase triangle for the transition between hydrated and anhydrous solid solution. In 12-57(c), the solubility curve is that of the continuous hydrated solid solution, since this temperature is below the curve pp' ; again the region AA_1B_1B is a mixture of two solid solutions — one on the line AB , the other on A_1B_1 .

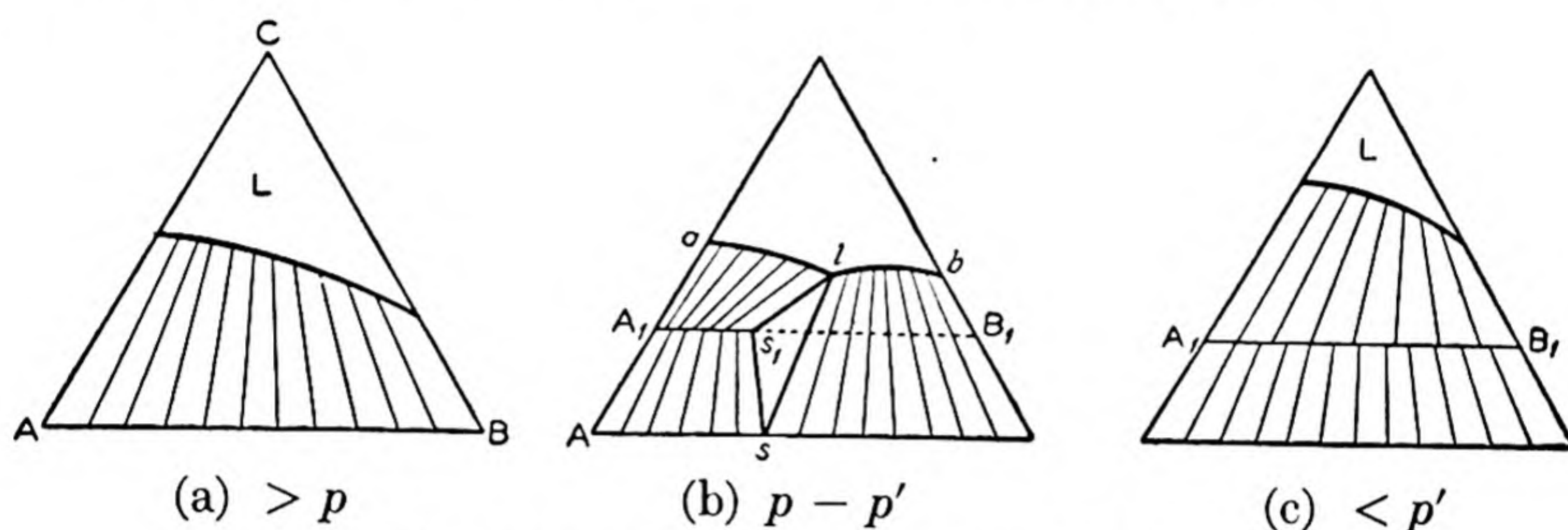


FIG. 12-57. Isotherms of Fig. 12-56.

Liquids in the region $App'B$ precipitate anhydrous solid solution S on cooling and reach the curve pp' to give the reaction $L + S \rightarrow S_1$ (hydrated crystals) + cals. If the original composition is in the trapezoid AA_1B_1B the liquid is consumed on the curve pp' to leave $S + S_1$; otherwise the hydration is completed, and the liquid, carrying S_1 , crosses to the eutectic curve ee' where it solidifies to ice + hydrated crystals.

In the vertical section (Fig. 12-56(c)) point p represents the binary transition or peritectic point for the reaction $A_1 + \text{cals.} \rightleftharpoons L + A$, isobarically invariant. But the hydrated solid solution x , decomposing into $L + \text{anhydrous solid solution}$, has a **transition range**, from t_1 to t_2 , for the equilibrium $S_1 + \text{cals.} \rightarrow L + S$, since it is ternary. For the compositions of the three phases during the transition, reference must be made to the course of the 3-phase transition triangle ls_1s of Fig. 12-57(b), between the temperatures t_1 and t_2 . At the initial temperature t_1 , the total composition is a hydrated solid solution, S_1 , at the point s_1 of this triangle, at t_1 . As T rises to t_2 , the triangle moves to the left and the original, fixed total composition comes to be swept by the line ls when the transition is complete, at t_2 , leaving the system $L + S$. The compositions of these phases then undergo further change, as parts of a 2-phase system, in accordance with the effect of T on the tie-lines of Fig. 12-57(a).

Just as the liquid-solid equilibrium of the binary system $A-B$ may have a maximum or a minimum, similarly the transition curve pp' of Fig. 12-56(a) may have a maximum or a minimum of temperature in it. This would be reflected by a maximum or minimum in the $L + S + S_1$ region of the

section 12-56(c), and in terms of the isotherm of 12-57(b) it would be a point at which the three phases of the transition triangle are colinear, while the salt-ratios of the two solid solutions would not necessarily be the same.

If there should be a number of corresponding hydrates forming continuous solid solutions, an intermediate isotherm may appear as in Fig. 12-58; again each hydrate is assumed to have an incongruent melting point in its binary system.¹⁴

b. If the anhydrous solid solution is continuous, and the hydrated discontinuous, there will be two ternary invariants. One of the possible arrangements is shown in Fig. 12-59. It is here assumed that the transition curves originating at p and p' both fall in T as they enter the ternary prism, and that the curve PE , running from their intersection P to the ice curve ee' , is of even reaction throughout. The result is a ternary eutectic E , but there are several other variations possible, including diagrams without a ternary eutectic. The A-rich hydrated solid is labeled α_1 , the B-rich β_1 . The invariant reaction at the ternary peritectic P is $L + S \rightarrow \alpha_1 + \beta_1 + \text{cals.}$; the

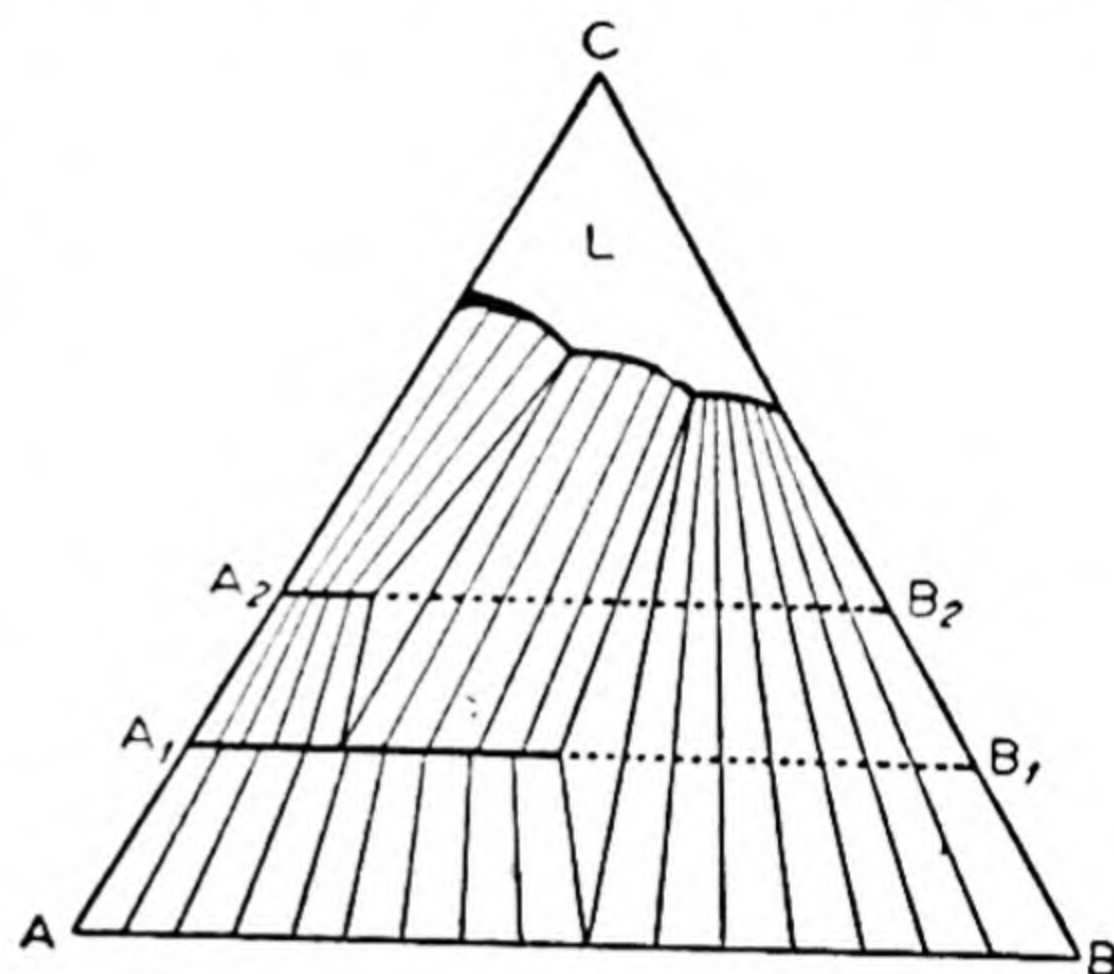


FIG. 12-58. Two degrees of hydration.

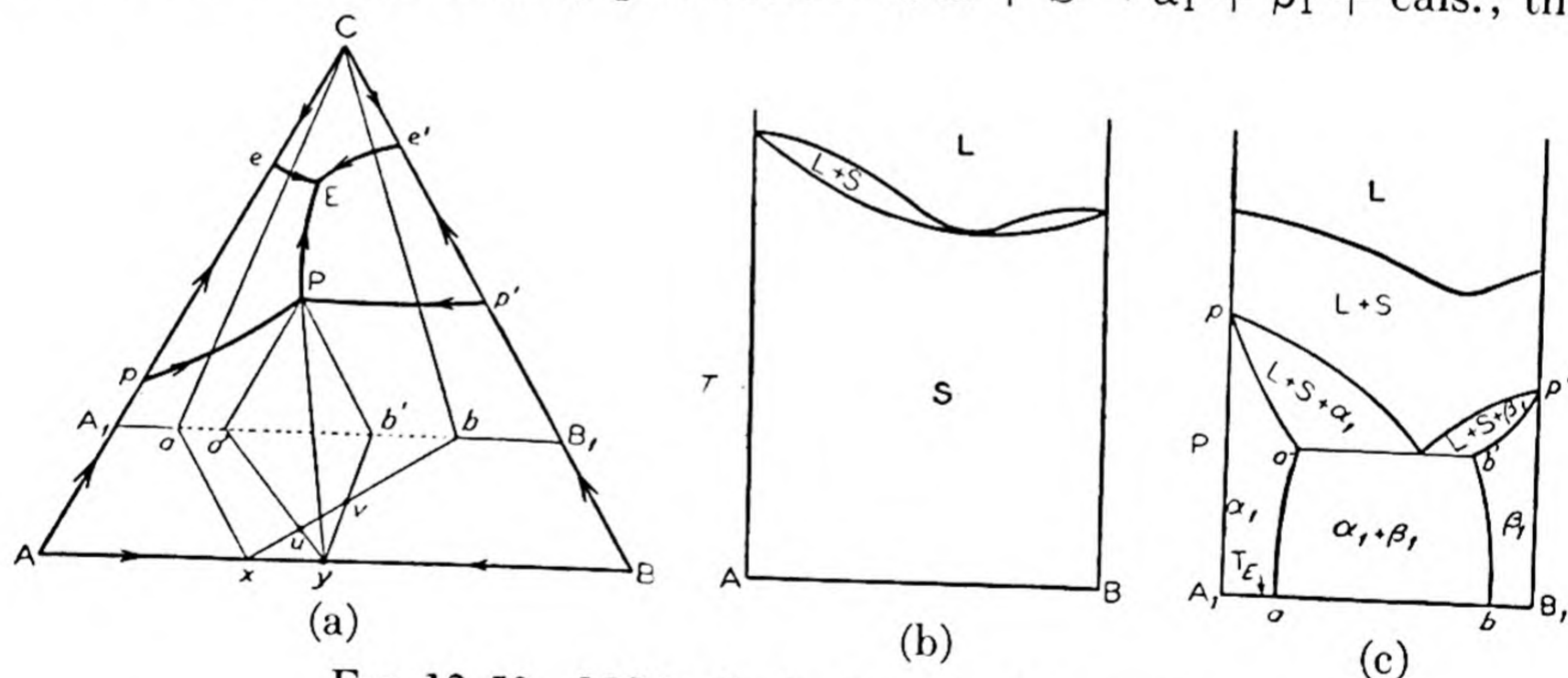


FIG. 12-59. MG in the hydrated solid solution.

compositions of S , α_1 and β_1 at this invariant are y , a' , b' of Fig. 12-59, respectively. At the eutectic the reaction is $L \rightarrow C + \alpha_1 + \beta_1 + \text{cals.}$, the hydrated solid solutions having the compositions of points a and b of Fig. 12-59. Liquids with original composition P in $ApPy$ (and similar con-

¹⁴ Cf. the 15°–25° isotherms for the system $\text{Na}_2\text{CrO}_4\text{--Na}_2\text{MoO}_4\text{--H}_2\text{O}$, W. E. Cadbury, *J. Am. Chem. Soc.*, 67, 202 (1945).

siderations apply to $Bp'Py$) precipitate anhydrous solid solution S on cooling, the liquid reaching the curve pP to give the reaction $L + S \rightarrow \alpha_1 + \text{cals.}$ Now with P in $AA_1a'y$ the liquid is consumed on the curve pP , to leave S on Ay and α_1 on A_1a' . With P in A_1pPa' , S is consumed, and the liquid, carrying α_1 , travels across the α_1 field, $peEP$, to one of the two curves eE and PE . The curve eE is reached if P is anywhere in the region A_1aEC ; moreover, then, if P is in the triangle A_1aC , the liquid is consumed on the curve eE to leave α_1 , on A_1a , + C .

The invariant point P is reached only by liquids with original compositions in the invariant quadrangle $a'Pb'y$. For those in $a'b'y$, P is an incongruent crystallization end-point, leaving the three solids $a' + b' + y$; for those in $a'Pb'$ the anhydrous solid y is consumed at P , and the liquid continues on curve PE to the eutectic. During this course, the conjugate,

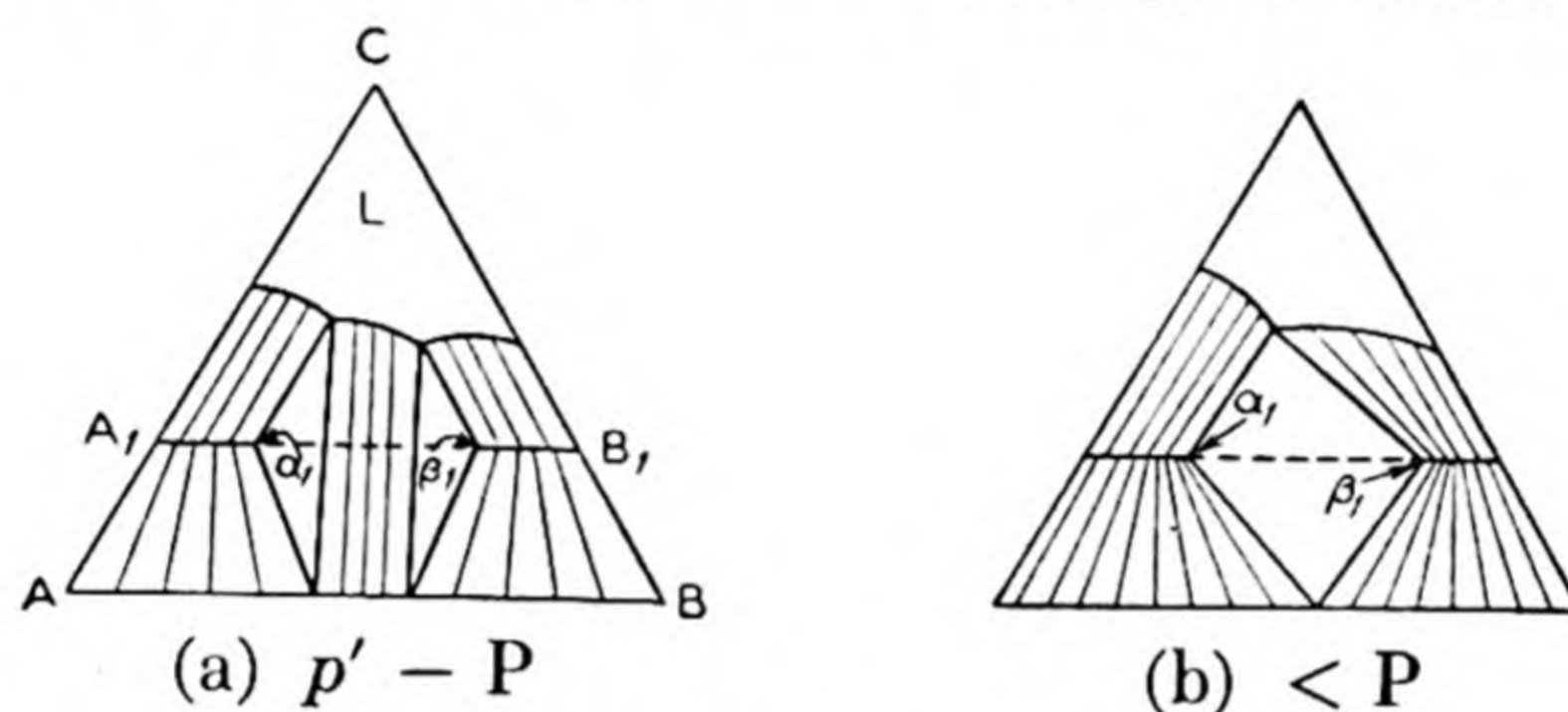


FIG. 12-60. Isotherms of Fig. 12-59.

hydrated solid solutions change in composition, to reach the points a and b at the eutectic temperature. Because of these changes in the miscibility gap of the hydrated solid solution, a 2-phase mixture in the region between the lines $a'y$ and ax may come to be swept by the line $a'y$ with falling T , and become a 3-phase mixture. A 3-phase mixture in the triangle uvy , on the other hand, may come to be swept by the line $b'y$ (moving to bx) with falling T and become a 2-phase mixture. The eutectic E is reached, of course, only by compositions in the eutectic triangle aCb .

Two schematic isotherms, which may be considered to be preceded by those of Fig. 12-57(a and b), are shown in Fig. 12-60. Again the limits α_1 and β_1 , in Fig. 12-60(a), represent not limits of a miscibility gap, as they do in Fig. 12-60(b), but simply corners of the 3-phase transition triangles, between hydrated and anhydrous solid solution. If the hydrates form no solid solution at all, the points α_1 and β_1 are always simply the points for pure A_1 and B_1 respectively, and we have the isotherms shown in Fig. 12-61, which are preceded by 12-57(a).

c. If the hydrated solid solution is continuous, the anhydrous discontinuous, the relations involve a ternary peritectic but no eutectic; Fig. 12-62 shows one of the possible arrangements. Here a and b represent the

MG in the system A-B at the binary eutectic e_1 and the points a' and b' represent the MG at the temperature of P, where the invariant reaction is $L + a' \rightarrow y + b' + \text{cals.}$ On complete solidification, all compositions in triangle A_1CB_1 consist of two solids, C (ice) + hydrated solid solution on

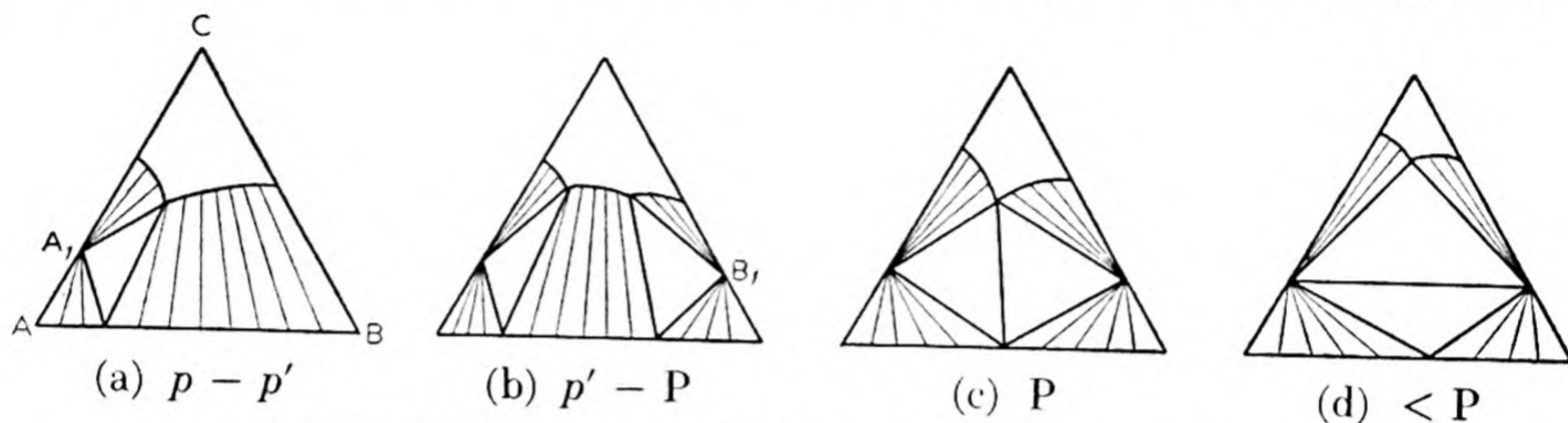


FIG. 12-61. Isotherms of Fig. 12-59 with pure hydrates.

the line A_1B_1 . Those in the two regions AA_1ya' and BB_1yb' similarly consist of two solids, an anhydrous solid solution and a hydrated solid solution. Those in the triangle $a'b'y$ consist of three solids of these compositions.

The invariant point P is reached only by liquids originally in the quadrangle $a'yPb'$. Those in yPb' lose the solid a' and travel on the curve Pp' toward p' ; but before p' is reached, either the liquid or the anhydrous solid solution, on Bb' , is consumed, because the triangle lyb' must collapse to

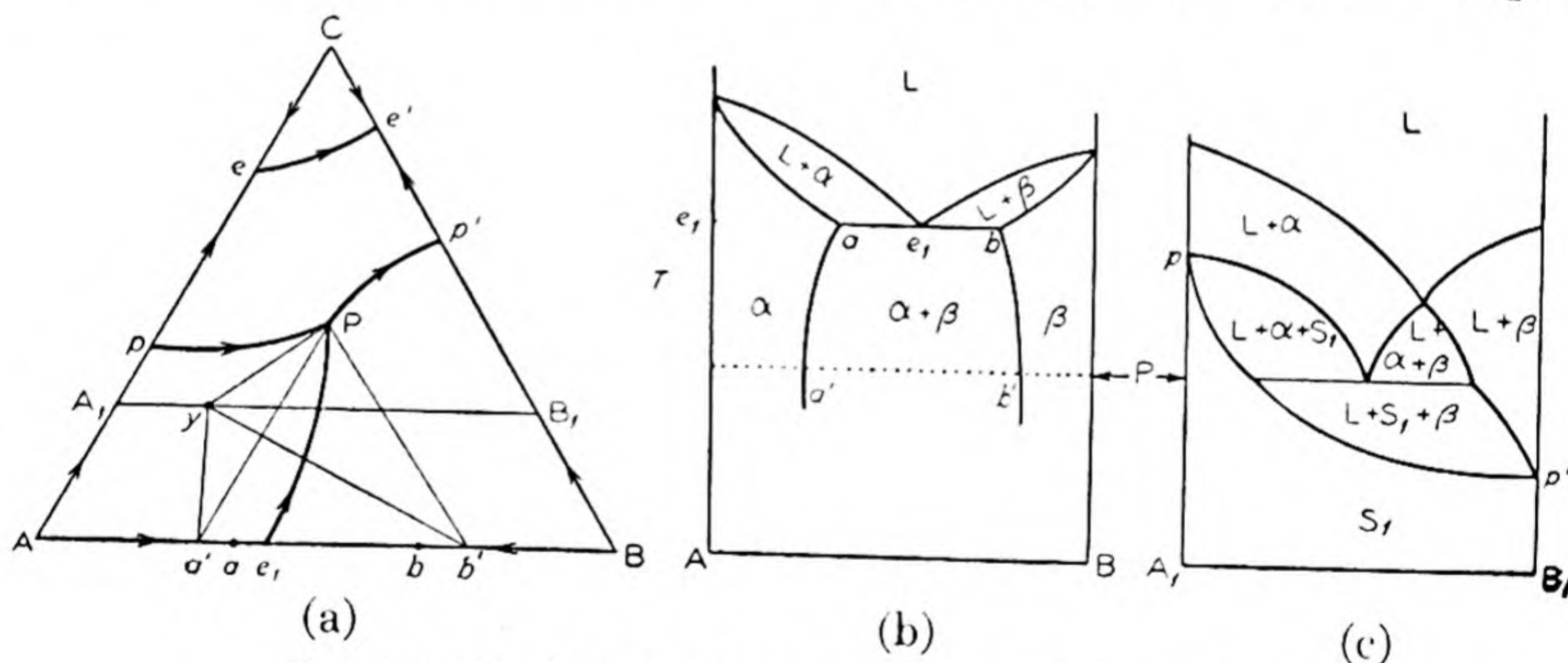


FIG. 12-62. MG in the anhydrous solid solution.

the line $p'B_1B$ at the BC side of the system. For compositions on the C side of yB_1 the anhydrous solid solution is consumed, and the liquid leaves the transition curve, being saturated with hydrated solid solution alone, and proceeds to the eutectic curve, on which it finally solidifies to $C + S_1$. For compositions below yB_1 the liquid is consumed, leaving a mixture of two solids, one on the line yB_1 and one on $b'B$. Compositions in $a'yb'$ lose their liquid phase at P, which is therefore the incongruent crystallization end-point for this region.

Schematic isotherms are shown in Fig. 12-63. In these isotherms the limits of the anhydrous solid solution, excepting points s in Fig. 12-63(b

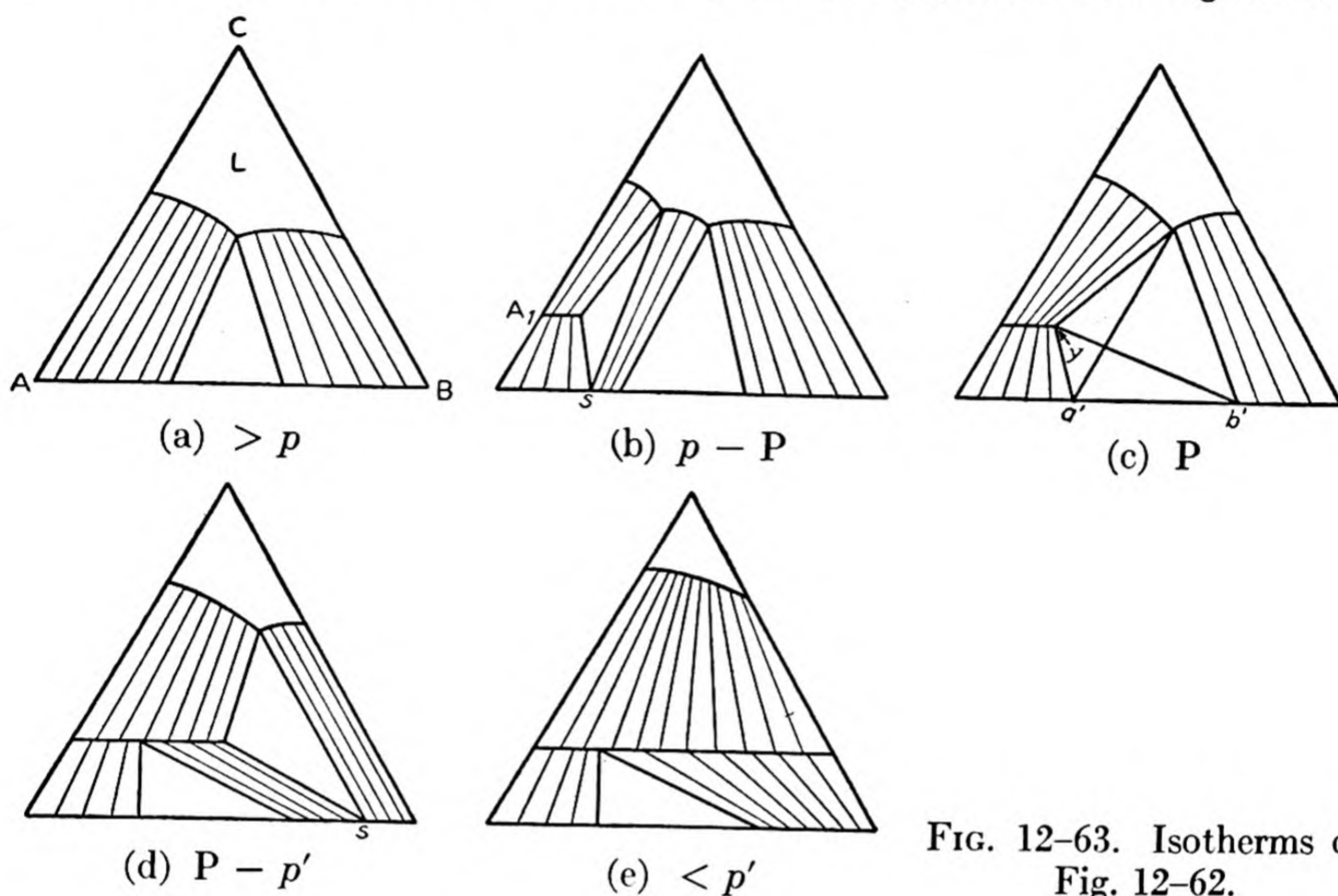


FIG. 12-63. Isotherms of Fig. 12-62.

and d), are points on the MG , but those of the hydrated solid solution are merely corners of the transition triangle. Finally, if the anhydrous salts are always pure, forming no solid solution whatever, the isotherms appear as in Fig. 12-64, preceded by 12-55(a).

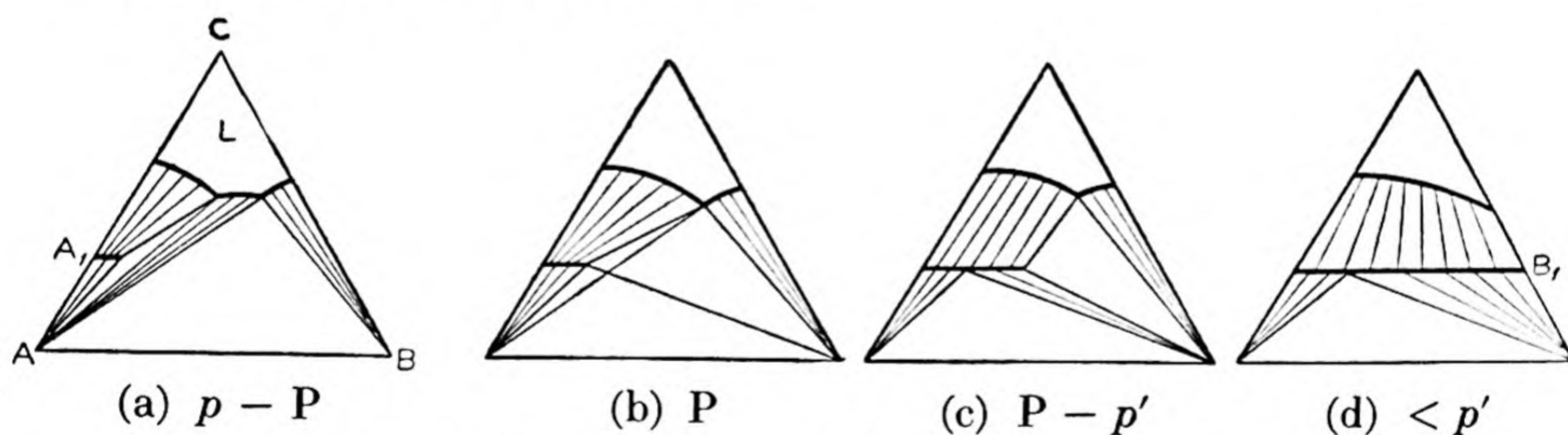


FIG. 12-64. Isotherms of Fig. 12-62 with pure anhydrous salts.

E. Ternary Compounds

1. With Congruent Melting Point

The crystallization field of a ternary compound, D , lies entirely inside the composition triangle, and the crystallization paths radiate, as straight lines, from the point representing its composition. If, at the pressure of the T/c prism, the ternary compound melts to a liquid of its own composition, it is

called **congruently melting**, or it is said to possess an **open maximum** (of temperature) on its crystallization surface. The maximum temperature of its field, for the equilibrium $L + D$, will, in other words, be at the point D itself, which lies within the field, with crystallization paths radiating from D in all directions (with falling T), as in Fig. 12-65(a). In this figure, D is assumed to be stable below the lowest eutectic of the system, so that there are three triangles of three solids for the completely solidified system: ADB , BDC , and CDA . There will then be three crystallization end-points; all these are here assumed to be congruent end-points or eutectics. The temperature on each curve of twofold saturation therefore falls to each eutectic, and the points m_1 , m_2 , and m_3 are maxima, or saddle points, on the curves E_1E_2 , E_2E_3 , and E_3E_1 , respectively. In this case, then, D is always

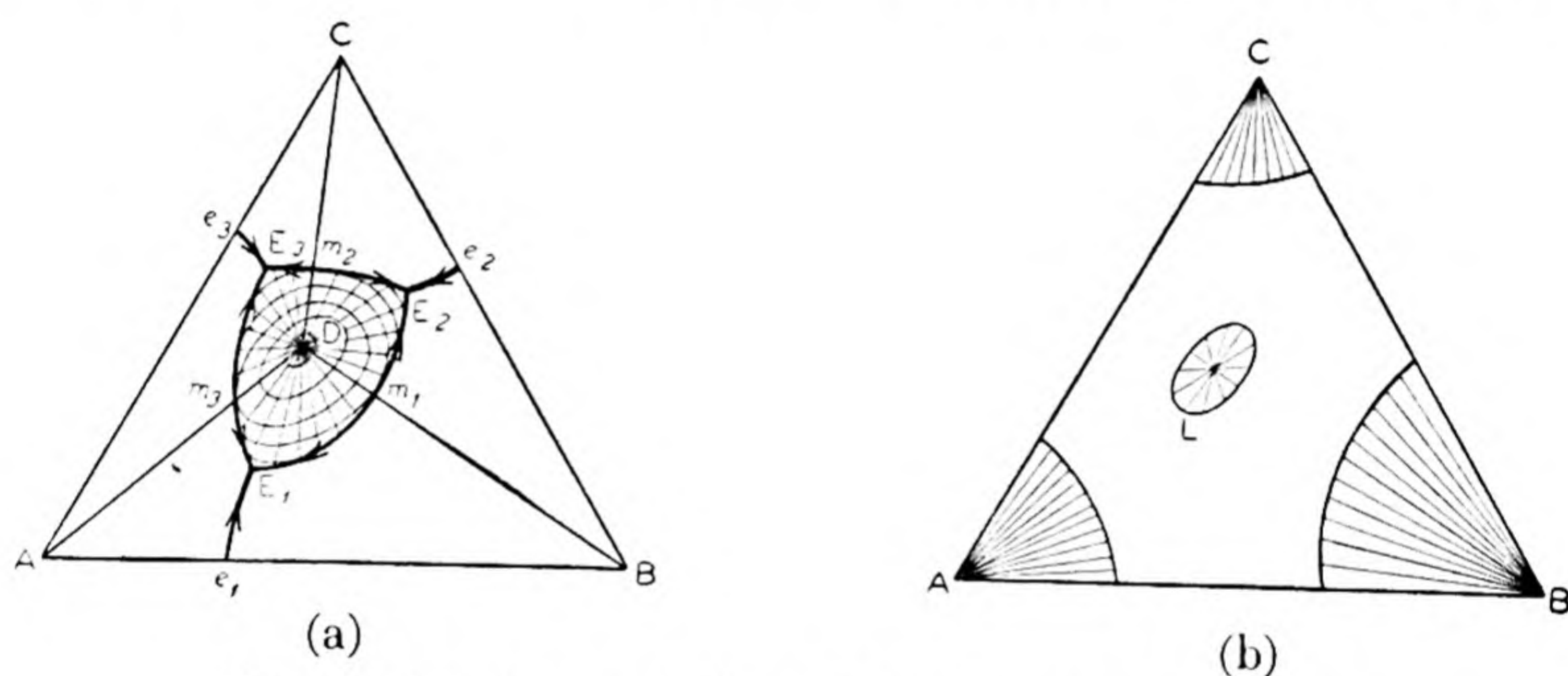


FIG. 12-65. Congruently melting ternary compound.

congruently soluble in each component, and the whole system is essentially the juxtaposition of three simple ternary systems each with its own eutectic point — as long as vapor equilibria are not involved. In other words, all the sections AD , BD , and CD are quasi-binary. If the melting point of D is below those of the three components but above the binary eutectics e_1 , e_2 , and e_3 , then an isotherm just below D has the appearance of Fig. 12-65(b). With tie-lines radiating from point D , we have here a closed, isothermal solubility curve of D in the ternary liquid.

The congruent melting point of D , for the system of condensed phases in absence of vapor, is an invariant equilibrium at an arbitrarily specified, constant pressure; at arbitrary P , D melts completely to L of the same composition, at an inherently constant temperature. For a ternary system at constant P , we have here $F = \alpha - \beta + 1 = 3 - 2 + 1 = 2$. But the identity of composition of solid and liquid involves two composition restrictions, for a ternary system has two independent composition variables and both must have the same value, in this equilibrium, for solid and liquid.

Hence $F = 0$ at constant P . But this is seen, perhaps more simply, to be an isobarically invariant equilibrium of a (quasi-) one-component system in two phases.

With vapor present, $F = 3 - 3 + 2 = 2$. Now again $F = 0$, because of the composition restrictions, but the system is a singular point (type m) of the ternary 4-dimensional diagram, not a physically invariant system, since the vapor composition although unique, differs from that of the liquid and the solid.

Variations of Fig. 12-65(a) are possible, if not all the three invariants are eutectics. In Fig. 12-66(a), for example, the relations in the triangle CDB

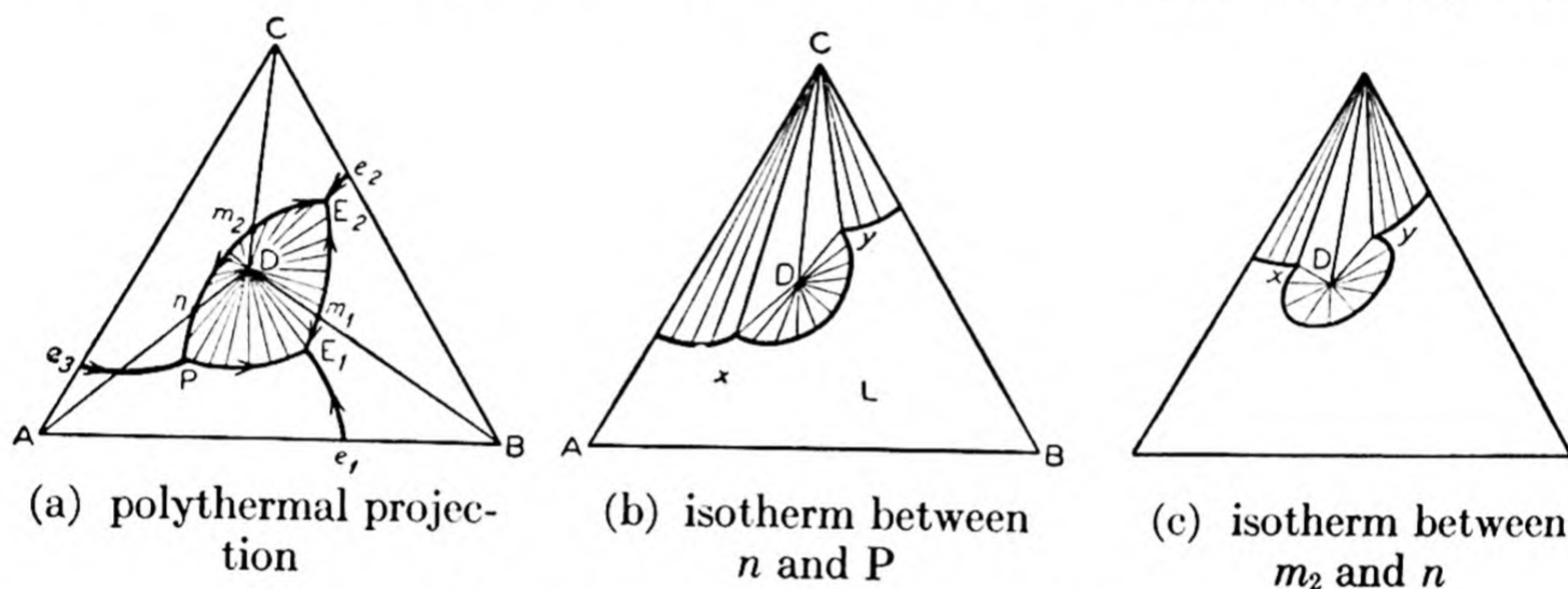


FIG. 12-66. Variation of Fig. 12-65.

are still the same; both the sections BD and CD are quasi-binary, and m_1 and m_2 are still saddle points. D is always congruently soluble in B and in C; in A, it is so only down to the temperature of n . If the temperatures of P, n , and m_2 are $\gg E_2$, m_1 , and E_1 , an isotherm between n and P may appear as in Fig. 12-66(b), and one between m_2 and n as in 12-66(c). The points x and y merge at m_2 , leaving an isotherm of the form of Fig. 12-65(b). The point P is now peritectic, type B, the invariant quadrangle being ACDP, and it is the incongruent crystallization end-point for the triangle ACD. The equilibria leading to P from high T are L, A+, C+, on curve e_3P , and L, C+, D+, on m_2P (possibly becoming odd, as L, C-, D+, near P). Those leaving P with falling T are L, A+, D+ on PE_1 , and the 3-solid equilibrium A + C + D.

If the system involves a binary compound D' besides the ternary compound D, some possible relations are shown in Fig. 12-67 (polythermal projections). There are two arrangements (a, b and c, d) of combinations of solids for complete solidification. In 12-67(a) and (c) all four invariants are assumed to be eutectics and hence congruent solidification end-points. In 12-67(b) and (d) one of the invariants (P) is a peritectic, a diagonal invariant of type B. In 12-67(b) it involves the solids A, D and D' in the

reaction $D + L(P) \rightarrow A + D' + \text{cals.}$, and it is therefore the incongruent crystallization end-point for compositions in the triangle ADD' . In 12-67(d) the invariant reaction is $D' + L(P) \rightarrow D + B + \text{cals.}$, and point P is the incongruent solidification end-point for the triangle $DD'B$.

Referring to Figs. 12-32 and 12-33 we note that each additional binary compound in the ternary system normally adds one invariant point in the

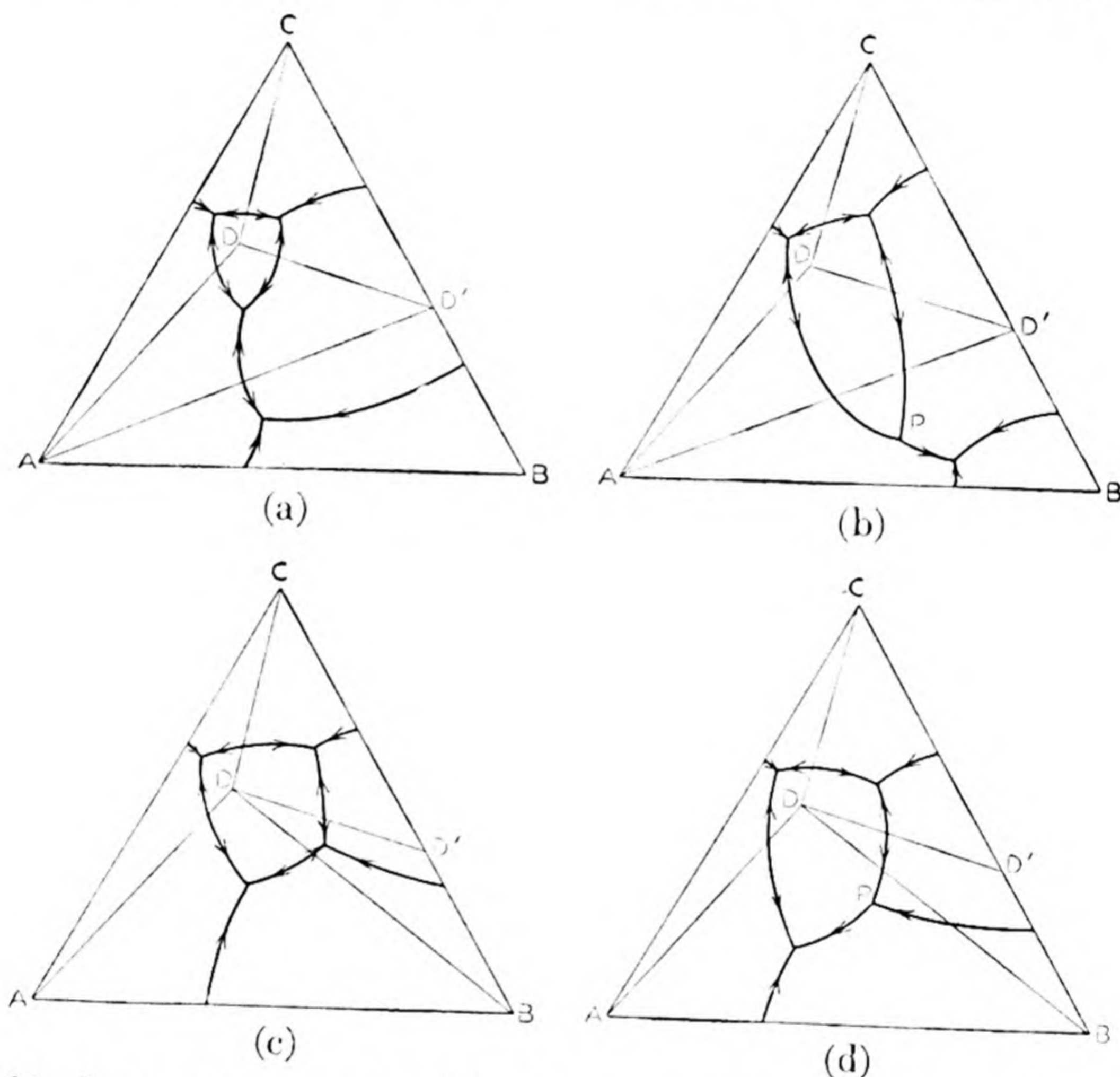


FIG. 12-67. Some arrangements with two compounds, one binary and one ternary.

solid-liquid equilibria and one 3-solid triangle in the division of the system for complete solidification; each additional ternary compound, on the other hand, adds two invariants and two triangles.

2. With Semicongruent Melting Point

There are two grades of incongruent melting for a ternary compound or for one not possessing an open maximum. If the compound is not congruently melting, the point D lies outside the D field, as in Figs. 12-68 and 12-69. In Fig. 12-68(a), in which the melting may be called **semicongruent**, the maximum temperature of the D field, or of the equilibrium $L + D$, is point m , fixed by the extension of CD with the (odd) curve L , $C-$, $D+$, running between P_1 and P_2 . When solid D is heated, in absence

of vapor and at the pressure of the prism, it melts incongruently (decomposes), invariantly, at T_m , to a solution simultaneously saturated with both C and D, leaving $L + C$ when D is all consumed. This case is somewhat similar, therefore, to the incongruent melting point of a binary compound. At the incongruent melting point T_m , the points C, D, and m (the liquid) are on one isothermal line, and D does not exist in stable equilibrium above this temperature, either with liquid or with the solid components, for

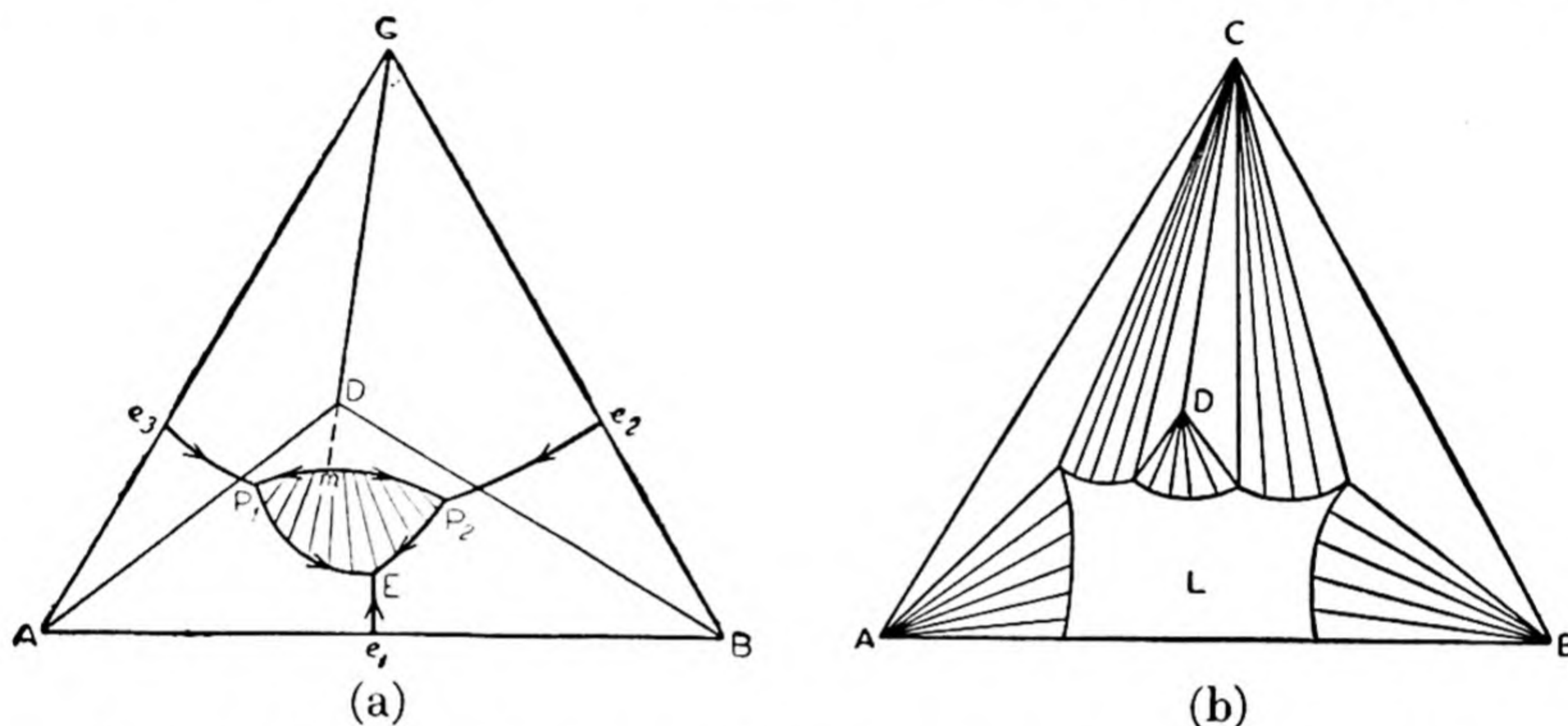


FIG. 12-68. Ternary compound with semicongruent melting point.

immediately above T_m we have the crystallization surface of C, or the equilibrium $L + C$, extending from Ce_3 to Ce_2 and up to the melting point of C. Fig. 12-68(b) is an isotherm just below T_m . The 2-phase tie-line area $D + L$ of this isotherm collapses to a line at T_m — part of the line CDm of Fig. 12-68(a) — and then the 2-phase tie-line area $C + L$ becomes continuous. The system of condensed phases $C + D + L(m)$ is invariant at arbitrary pressure because it is equivalent to a binary system in three phases, the binary system consisting of the components C and a mixture of A and B in the ratio present in D. As a ternary system at constant P , it has $\alpha - \beta + 1 = 1$ and hence $F = 0$ because of the (now single) restriction that one composition variable, namely, the ratio A/B , is the same in both D and L; the colinear relation of the compositions of the three phases C, D, and L constitutes, in other words, one composition restriction. With vapor present, this semicongruent melting point is no longer physically invariant, but only a singular point (type m) of the system.

3. With Incongruent Melting Point

In Fig. 12-69(a), the maximum temperature of the D field is an intersection of three curves of twofold saturation, at P_t . When solid D is heated, it melts **incongruently** (decomposes), invariantly at P_t , to a solution simul-

taneously saturated with three solids, C, A, and D, leaving $L + C + A$ when D is all consumed. Now D is the interior phase of the invariant 4-phase triangle (type A, therefore) CP_tA ; and the three equilibria originating at this point with falling T are $L, A-, D+$ on curve P_tE_1 , $L, C-, D+$ on curve P_tE_2 and the 3-solid equilibrium $A + C + D$. The curves P_tE_1 and P_tE_2 , however, both become even ($A+, D+$ and $C+, D+$) before reaching

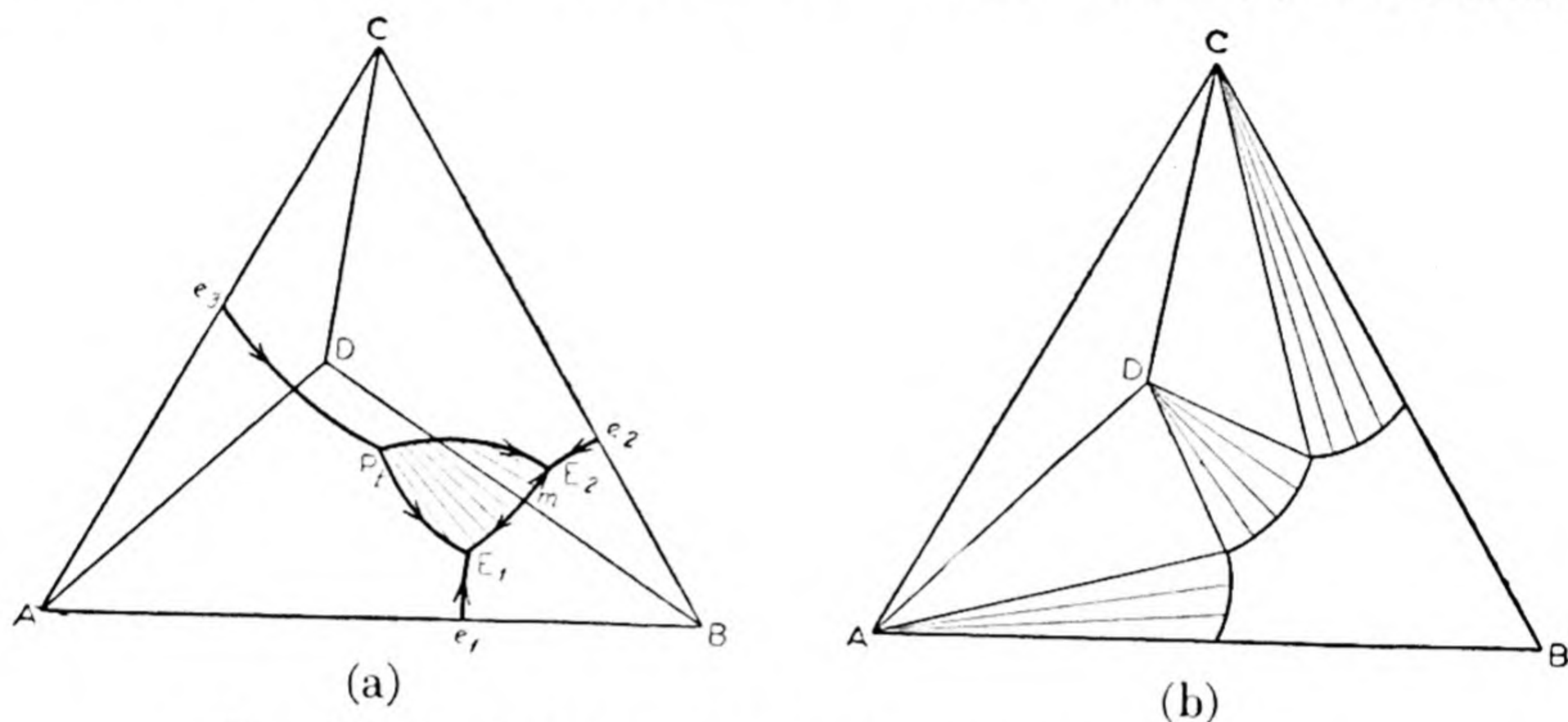


FIG. 12-69. Incongruently melting ternary compound.

the eutectics. An isotherm between P_t and the saddle point m is shown in Fig. 12-69(b). With vapor present, the decomposition of D into L, C, and A, is a true, physically invariant equilibrium in five phases.

In all these cases (Figs. 12-65 to 12-69) the crystallization paths in the D field radiate from the point D, whether or not this point is inside the D field. The extrapolation of a number of such paths to a point of intersection may therefore be used to fix the composition of the compound, as explained under Fig. 12-5; (cf. Ref. 1 of this chapter, for examples involving ternary compounds).

4. Examples

For ternary compounds with "open maxima" or congruent melting points, we may cite Mg_4Al_6Cu in the system Mg-Al-Cu,¹⁵ $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ in the system K_2SO_4 - $MgSO_4$ - H_2O ,¹⁶ and $FeCl_3 \cdot HCl \cdot 4H_2O$, melting at -3° , in the system $FeCl_3$ - HCl - H_2O . The crystallization field of this last compound is an interesting one, with boundaries on those of nine other solid phases: $FeCl_3 \cdot HCl \cdot 2H_2O$, $FeCl_3 \cdot 2H_2O$, $2FeCl_3 \cdot 5H_2O$, $2FeCl_3 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, $FeCl_3 \cdot HCl \cdot 6H_2O$, $HCl \cdot 3H_2O$, $HCl \cdot 2H_2O$, and (although not experimentally determined) $HCl \cdot H_2O$.¹⁷ The com-

¹⁵ R. Vogel, *Z. anorg. Chem.*, **107**, 265 (1919).

¹⁶ J. K. van der Heide, *Z. phys. Chem.*, **12**, 416 (1893).

¹⁷ B. Roozeboom and F. A. H. Schreinemakers, *Z. phys. Chem.*, **15**, 588 (1891).

pound $\text{Al}_2\text{Mg}_3\text{Zn}_3$,¹⁸ also congruently melting, forms ternary solid solution with its components, so that it is the ternary analog of the binary compound in Fig. 7-43.

The case of Fig. 12-68, or semicongruent melting, is exemplified by the ternary compound carnallite,¹⁹ $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Fig. 12-70, schematic).²⁰ At 167° (T_m of Fig. 12-68(a); point m on Fig. 12-70), this compound decomposes into KCl and the solution m , and the system remains

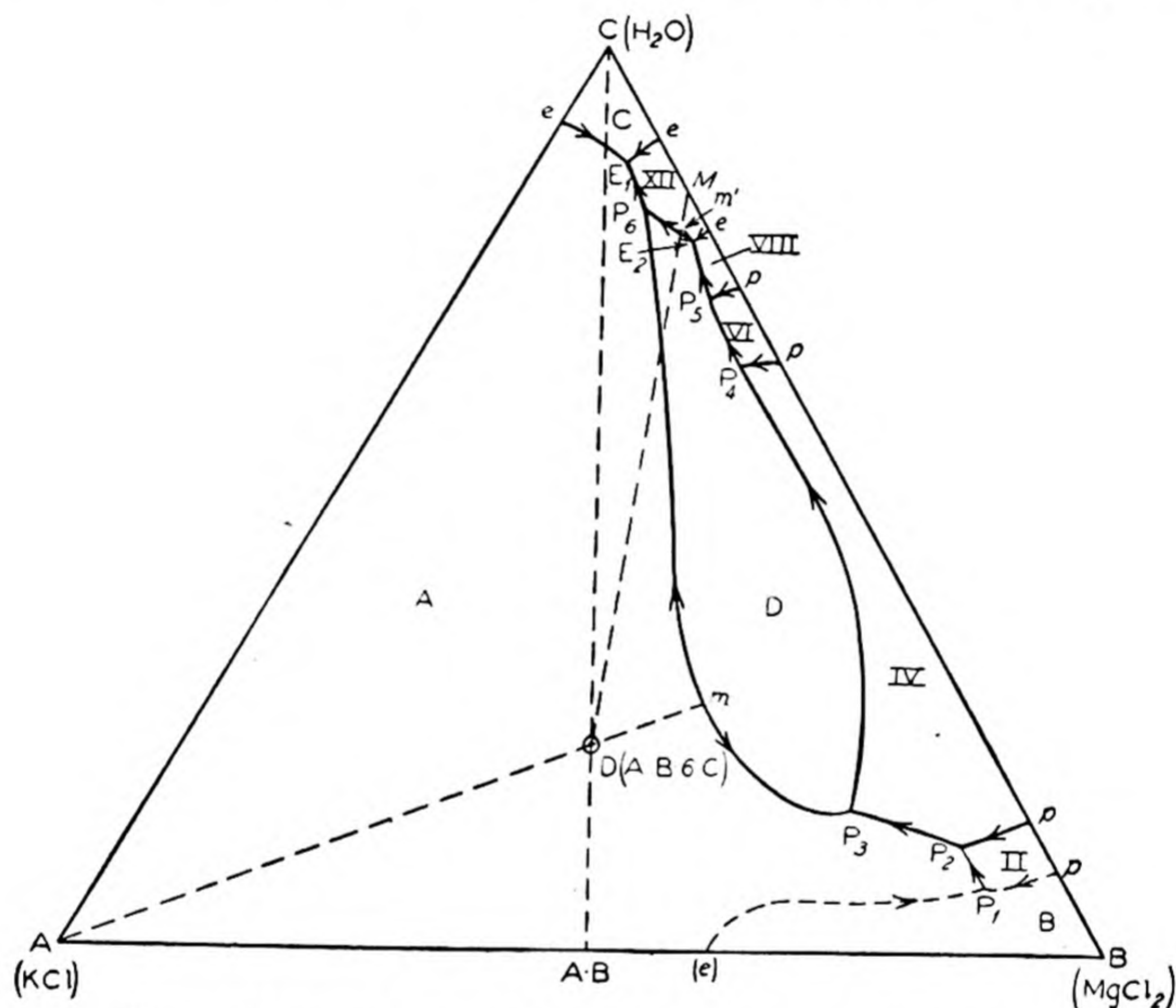


FIG. 12-70. System $\text{KCl}-\text{MgCl}_2-\text{H}_2\text{O}$ (schematic).

invariant (always provided that the vapor phase is not involved) until all the carnallite is consumed. The crystallization fields of Fig. 12-70 are marked for the phases as follows: A(KCl), C(ice), B(MgCl_2), D(carnallite), and II, IV, VI, VIII, XII for the hydrates of MgCl_2 . The first four hydrates melt incongruently, the binary peritectic points being marked $p \cdots p$. The dodecahydrate melts congruently ($M = -16.4^\circ$) and the four binary eutectics are marked $e \cdots e$. The points $P_1 \cdots P_6$ are ternary peritectics, while E_1 and E_2 are ternary eutectics, E_1 (at -34.3°) for the phases $\text{KCl} + \text{ice} + \text{XII}$ in the triangle ACM , and E_2 (at -16.9°) for the phases

¹⁸ W. Köster and W. Dullenkopf, *Z. Metallkunde*, **28**, 367 (1936).

¹⁹ J. H. van't Hoff and W. Meyerhoffer, *Z. phys. Chem.*, **30**, 86 (1899).

²⁰ Another example is $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ in the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, decomposing at $\sim 1470^\circ$ to liquid + solid $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, itself an incongruently melting binary compound in the system $\text{Al}_2\text{O}_3-\text{SiO}_2$; *I. C. T.*, IV-92.

D + XII + VIII. The point m' , the intersection of DM with the curve E_2P_6 , is a maximum (saddle point) on this curve (at -16.8°), P_6 being at -21° . The point m , for the decomposition of carnallite, is a maximum on the curve P_3P_6 , but not a saddle point, since the temperature falls away from the curve, at m , into the carnallite field.

A simple example of the incongruent melting type of Fig. 12-69 is found in the system $\text{Na}_2\text{SO}_4\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ (Fig. 12-71, schematic).²¹ The

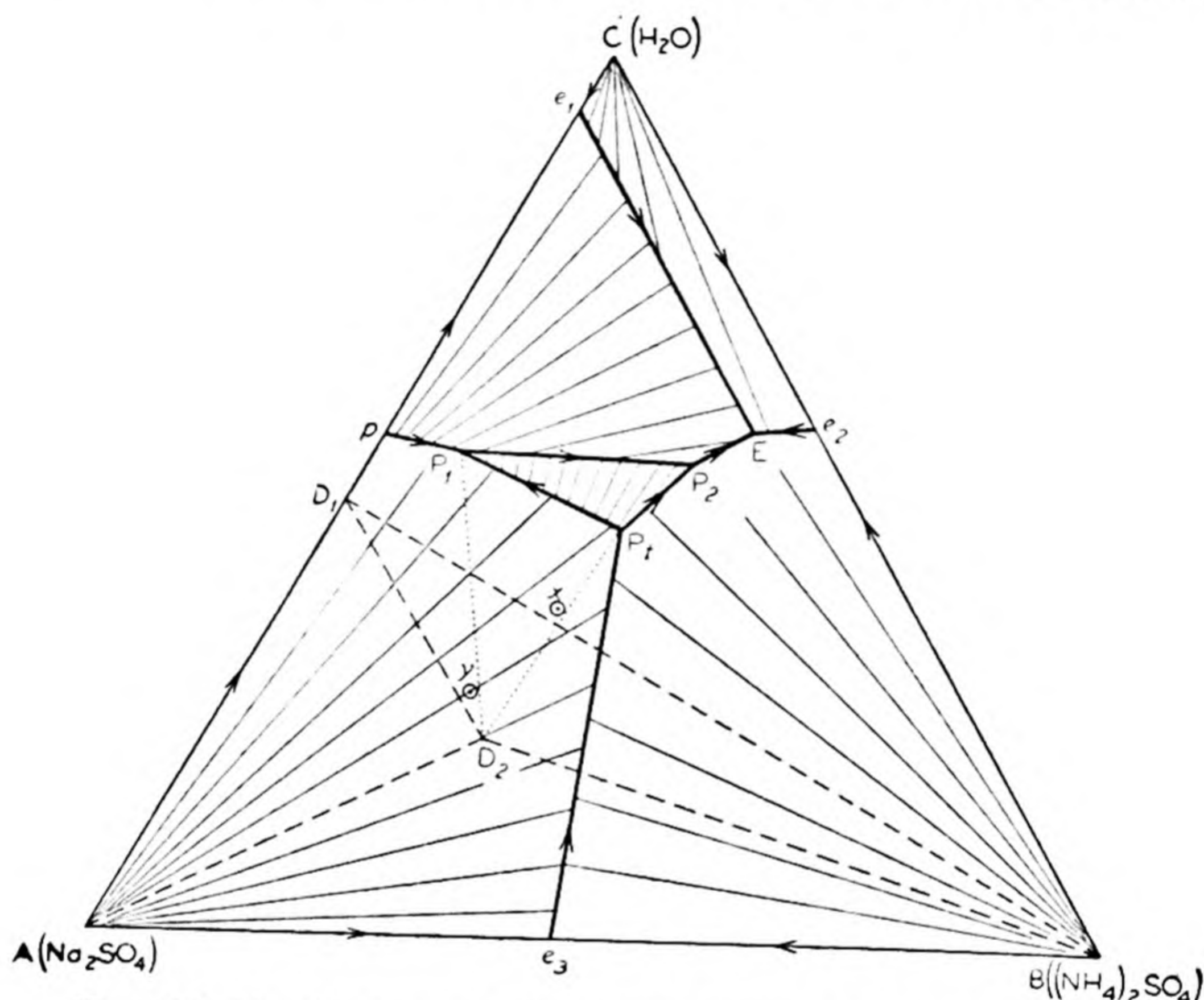


FIG. 12-71. System $\text{Na}_2\text{SO}_4\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ (schematic).

binary compound D_1 , or $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, is incongruently melting, with a binary transition point at p . The ternary compound D_2 , $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, first appears on cooling at the ternary invariant point P_i (type A) in the reaction $A + B + L \rightarrow D_2 + \text{cals.}$, or, on heating, the compound melts incongruently into liquid of composition P_i + the two solids Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$, at the constant temperature of $P_i (=59.3^\circ)$, a 5-phase, true invariant point in presence of vapor. P_i is reached by all liquids in AP_iB , on cooling. Those from the triangle AD_2B solidify completely at P_i as their incongruent crystallization end-point. Those from the triangle AP_iD_2 lose the B phase, to travel on the curve P_iP_1 , with the odd reaction $A - , D_2 +$; and those from D_2P_iB lose solid A at P_i and proceed along the curve P_iP_2 with the reaction $B - , D_2 +$.

²¹ I. C. T., IV-333, 389; A. Seidell, *Solubilities of Inorganic and Metal Organic Compounds*, D. Van Nostrand, N. Y., 1940; p. 1125.

Point P_1 (type B), involving the invariant reaction $A + L \rightarrow D_1 + D_2 + \text{cals.}$, is reached by all liquids in the quadrangle $AD_1P_1D_2$. It is the incongruent crystallization end-point for the triangle AD_1D_2 . Otherwise solid A is consumed and the liquid proceeds along the curve P_1P_2 , with the odd reaction $D_2 -$, $D_1 +$. P_2 , also type B , is reached by all liquids in the quadrangle $D_1P_2BD_2$, and its reaction is $D_2 + L \rightarrow D_1 + B + \text{cals.}$ It is therefore the incongruent crystallization end-point for triangle D_1D_2B ; and otherwise the solid D_2 is consumed, to allow the liquid to travel on P_2E to the ternary eutectic E , which is also reached along the curves e_1E and e_2E , for the solids $D_1 + C + B$. The curves e_1E , e_2E , P_2E , and e_3P_t are curves of even $(++)$ reaction. The four others are all odd ($A -$, $D_1 +$ for pP_1), and all four may therefore be crossed during equilibrium solidification. The curve pP_1 is crossed by solutions reaching it from the triangle D_1pP_1 , while P_1P_2 is crossed by solutions from the triangle $D_1P_1P_2$. Curve P_tP_1 is crossed by solutions from the triangle $D_2P_1P_t$ and curve P_tP_2 by solutions from $D_2P_tP_2$.

Liquid x on cooling, therefore, forms solid Na_2SO_4 as primary crystallization product, and $(\text{NH}_4)_2\text{SO}_4$ as second product when it reaches the curve e_3P_t . At P_t the $(\text{NH}_4)_2\text{SO}_4$ redissolves at the expense of the compound D_2 . The solution then travels on the curve P_tP_1 until the Na_2SO_4 is also all consumed, leaving D_2 as sole solid phase. At this point (when the liquid is on a line with x and D_2) the liquid leaves the curve and crosses the D_2 field to the curve P_1P_2 , where $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} (D_1)$ begins to precipitate. Then as the liquid travels on the curve P_1P_2 toward P_2 , the double salt D_2 is being dissolved at the expense of D_1 . At P_2 , B reappears as solid phase and the rest of the D_2 is consumed. Now precipitating D_1 and B , the liquid continues on the curve P_2E to E , where ice appears, to leave a mixture of ice, $(\text{NH}_4)_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

Liquid y is interesting in that, with equilibrium crystallization, it passes successively through the invariant points P_t and P_1 before solidifying incongruently at P_2 as a mixture of D_1 , D_2 , and B . Again phase B , or $(\text{NH}_4)_2\text{SO}_4$, would appear as second crystallization product on curve e_3P_t , to disappear at P_t and reappear at P_2 .

F. Polymorphism

If one of the *pure* solids, such as C , has a polymorphic transition at a temperature in the range of its ternary solubility equilibria, that is, in the temperature range of its crystallization field, this field is divided into two parts by an isothermal curve of twofold saturation. The temperature of this transition curve is that fixed by the pressure of the T/c prism, for the component C in its (unary) transition $C_\alpha \rightleftharpoons C_\beta$. In Figs. 12-72 and 12-73,

the component C is assumed to have three such transitions, for four solid forms. The "C" field is therefore divided into four parts, by three isothermal curves of twofold saturation. The first, ll' , for $L + C_\delta + C_\gamma$, runs from one binary side to the other, since its temperature is above the adjacent binary eutectics e and e_2 . The second, $t_1l'_1$, for $L + C_\gamma + C_\beta$, is at a temperature between these eutectics, and therefore runs from the side AC to the e_2 eutectic curve. The third, $t_2l'_2$, for $L + C_\beta + C_\alpha$, being below e but above the ternary eutectic E, runs between two eutectic curves.

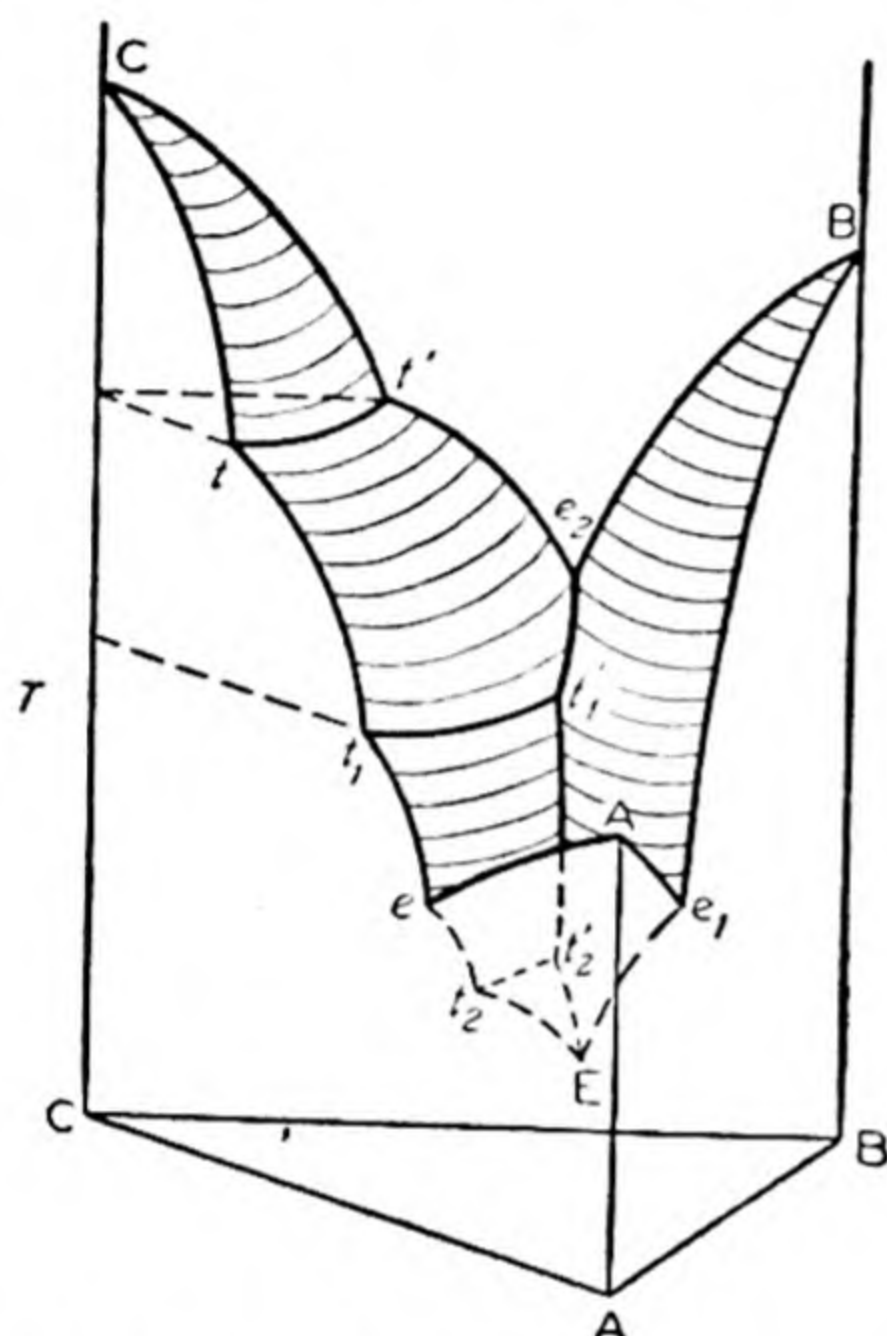


FIG. 12-72. Polymorphism of pure solid C.

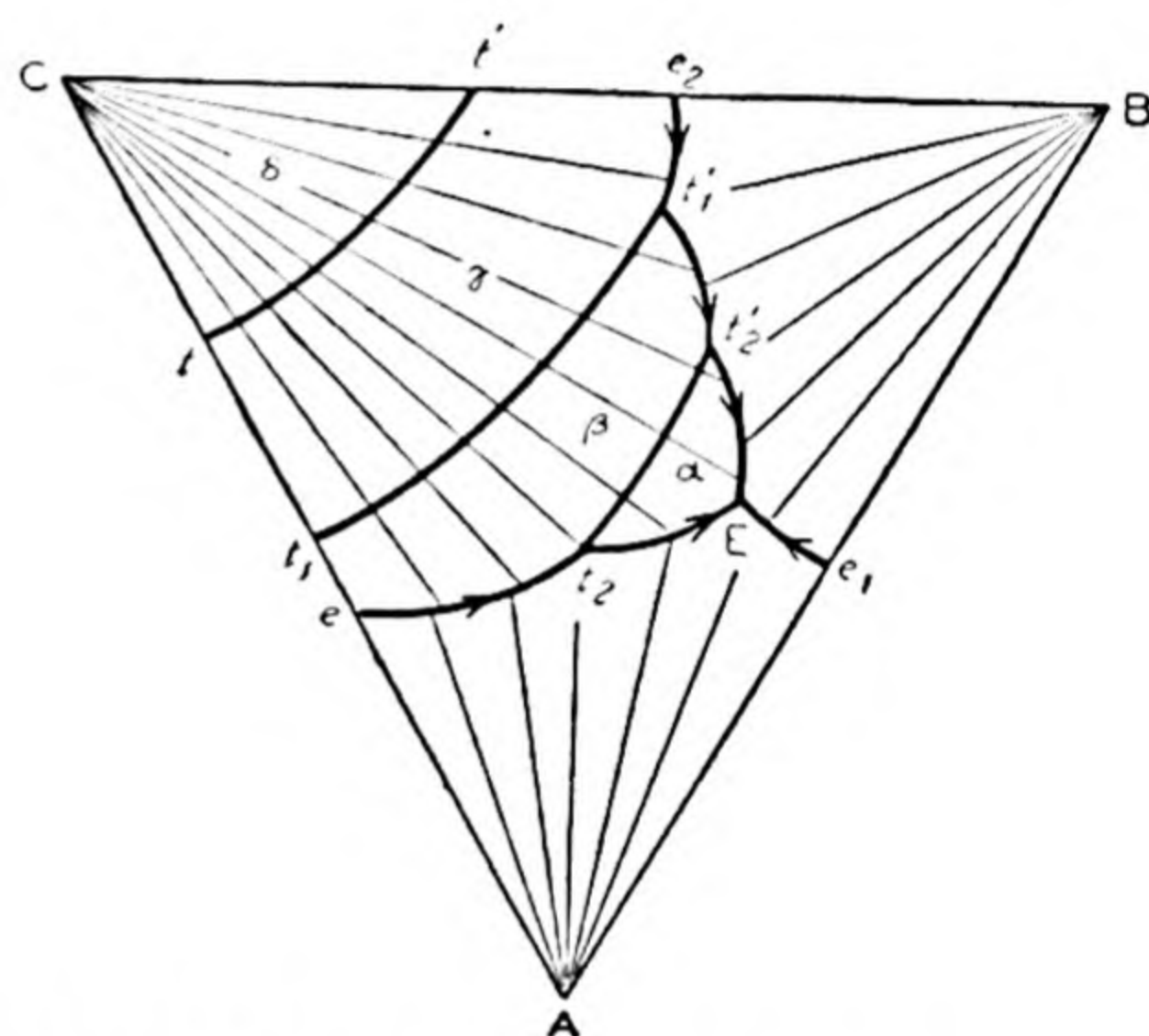


FIG. 12-73. Polythermal projection of Fig. 12-72.

These curves are isothermal, and any liquid reaching one during the course of solidification stops on the curve without traveling on it, until the polymorphic transformation of solid C has proceeded to completion; the liquid then crosses the curve to a surface of lower T . The system on such a curve is therefore invariant, either at arbitrary P or as a condensed system, although it consists of only three condensed phases, the liquid and two solids, because the phase reaction is one of lower order, involving only the component C. The *effective order* (cf. Chapter I, H-3) of the formally ternary system is therefore binary along the curves, but it is again ternary at the points l'_1 , l'_2 , t_2 , where a third solid phase appears; and the curves $e_2l'_1$, $l'_1l'_2$, l'_2E are three distinct curves, with breaks at their intersections, since there is a distinct change of one solid phase from one curve to another. In addition, we note again that the quantity of the liquid phase is constant during the polymorphic transformation along one of the isothermal curves.

The same applies for the polymorphism of compounds, binary or ternary. There will be a field for each form, and the curve of twofold satura-

tion, $L + \text{form } \alpha + \text{form } \beta$, separating two adjacent fields, is isothermal in the isobaric T/c relations.

An isotherm at a temperature just below $t_1t'_1$, where C_β is stable, would appear as in Fig. 12-74. Curve βx is the solubility curve of the stable form C_β , and point x is the isothermally invariant solution saturated with C_β and B. Curve γy is the solubility curve of the metastable (and therefore more soluble) form C_γ , and xy is an extension of bx , so that y is the metastable isothermally invariant solution saturated with C_γ and B. Since the curve $t_1t'_1$ of Fig. 12-73 is isothermal, the curves βx and γy never cross on any isotherm, as the stable and metastable solubility curves of hydrates do (cf. Fig. 12-38).

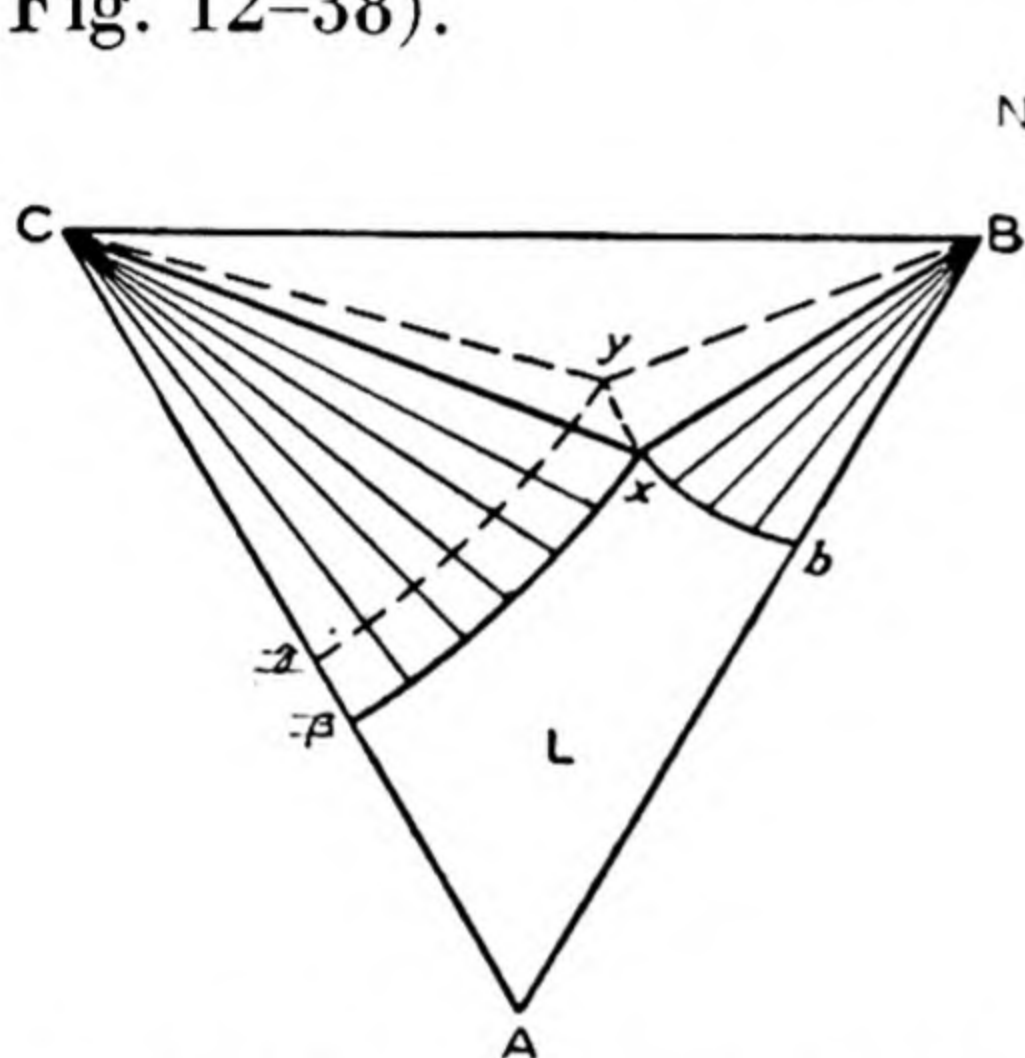


FIG. 12-74. Isotherm of Fig. 12-72, between t_1 and A, with $t_1 > A$.

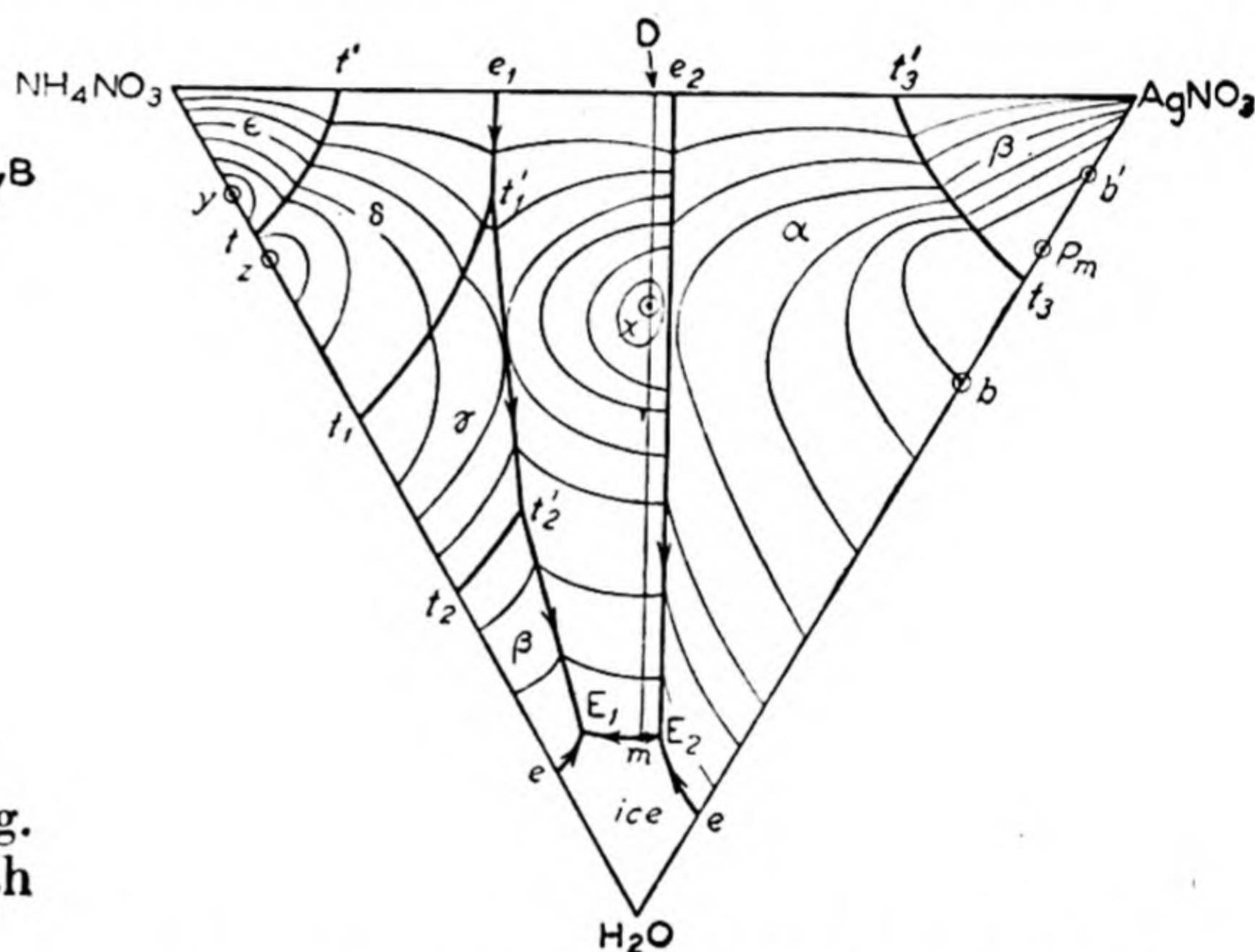


FIG. 12-75. System $\text{NH}_4\text{NO}_3\text{-AgNO}_3\text{-H}_2\text{O}$ (schematic).

Fig. 12-75 is the polythermal projection of the system $\text{H}_2\text{O-AgNO}_3\text{-NH}_4\text{NO}_3$, studied by Dingemans.²² The compound $\text{AgNO}_3 \cdot \text{NH}_4\text{NO}_3(\text{D})$ melts congruently, the section $\text{H}_2\text{O-m-D}$ is quasi-binary, and the line $m\text{D}$ is a ridge of maximum temperature for the D field, which is $e_1\text{D}e_2\text{E}_2m\text{E}_1$. The curves tt' , $t_1t'_1$, $t_2t'_2$ are isothermals, at 125° , 84° and 32° respectively, for the polymorphic transitions of pure NH_4NO_3 (cf. Figs. 2-10 and 6-11). Curve $t_3t'_3$ is similarly isothermal, at 160° , for the $\alpha \rightleftharpoons \beta$ transition of pure AgNO_3 . The direction of falling temperature is shown in the usual way on the curves for liquids of twofold saturation. In addition, however, this diagram is interesting in that it also shows vapor pressure contours for the saturated aqueous solutions.^{22a} Points b and b' on the $\text{H}_2\text{O-AgNO}_3$ side are both solutions with 760 mm of vapor pressure, and P_m is a saturated solution

²² P. Dingemans, *Rec. trav. Chim. Pays-Bas*, **62**, 85 (1943).

^{22a} On the vapor pressure of aqueous solutions saturated with two salts, see A. E. Korvezee, P. Dingemans and L. L. Dijkgraaf, *ibid.*, **66**, 389 (1947).

of maximum vapor pressure; these points are in fact those so labeled in Fig. 5-11. There is a similar maximum near x on the ridge mD , at ~ 80 mm, and two maxima, y and z , on the binary side $H_2O-NH_4NO_3$, at ~ 200 mm.

If the phase undergoing polymorphic transition is a solid solution, either binary ($C + A$) or ternary ($C + A + B$), then the transition curves of Figs. 12-72 and 12-73 are no longer isothermal. In the case of a ternary solid solution, in which the transition point $C_\alpha \rightleftharpoons C_\beta$ is lowered both by A and by B , a vertical section through C and the side AB would appear as in Fig. 12-76. This section would represent relations sweeping continuously from the CA to the CB side. The curve of the liquid of twofold saturation

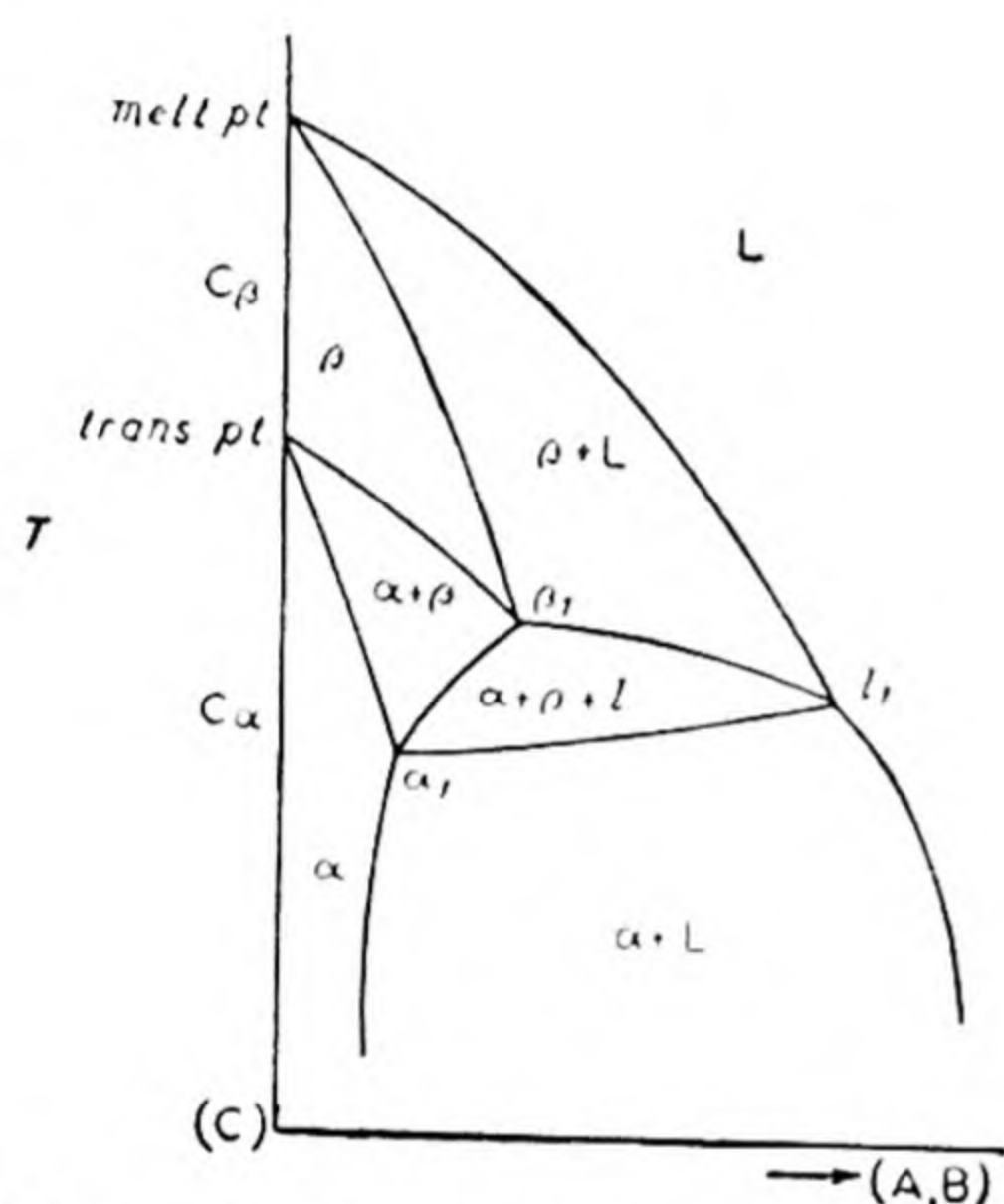


FIG. 12-76. Polymorphism of C , with ternary solid solution.

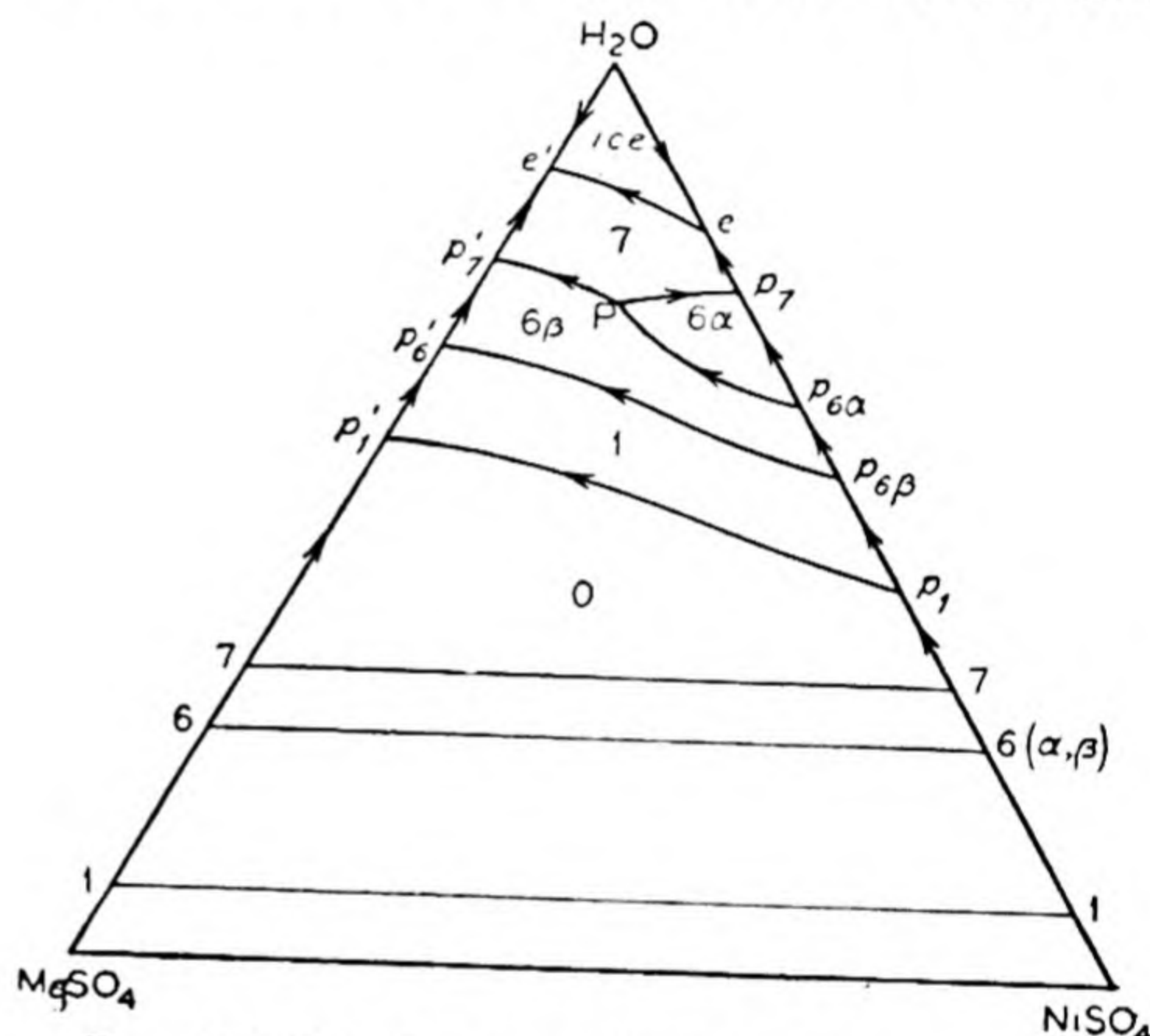


FIG. 12-77. System $MgSO_4-NiSO_4-H_2O$ (schematic).

($l + \alpha + \beta$) runs continuously from l on the CA side to l' on the CB side. The binary points are at different temperatures, and there may be a maximum or a minimum on the ternary transition curve ll' , where the coexisting phases α , β and l are colinear. In general the phases α and β of the region $\alpha + \beta + l$ of Fig. 12-76 are not on the plane of the section with l ; cf. Fig. 11-14. Moreover, if the transition point is lowered by B and raised by A , as would be the case in the system $Fe-C-Zr$ since carbon raises, zirconium lowers, the $\gamma \rightleftharpoons \delta$ transition temperature, the α and β curves, like the l and α curves of Figs. 11-19 and 11-20, would cross in isothermal projection, with reversal of the order of points α_1 and β_1 of Fig. 12-76, as in Fig. 11-20 (c, d) for l' and α' .²³ Finally, if the solid solution involves B but not A , then l is the transition temperature of pure C , with α_1 and β_1 there coincident with C , but the curve ll' is nevertheless not isothermal.

Fig. 12-77 is a schematic polythermal projection of a system involving

²³ R. Vogel (Ref. V), pp. 557-9. For detailed discussion of additional cases and variations, see Masing, (Ref. L), Chapters X and XI.

polymorphism of a hydrate. It is the system $\text{MgSO}_4\text{--NiSO}_4\text{--H}_2\text{O}$,²⁴ in which the salts form continuous solid solution both in the anhydrous condition and as hydrates (1, 6, 7). But whereas $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is dimorphic, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ is not. Curves $p_1p'_1$ and $p_{6\beta}p'_6$ connect corresponding incongruent melting points of the binary aqueous systems, and ee' connects the eutectics, as in Fig. 12-56(a); $p_{6\alpha}$ is the transition point $6\alpha \rightleftharpoons 6\beta$ in the binary system $\text{H}_2\text{O--NiSO}_4$. This transition follows the course $p_{6\alpha}P$ in the ternary system, with falling temperature; the liquid on this curve is in equilibrium with two forms of hexahydrated solid solution, and on cooling the β form is consumed at the expense of the α . At P the heptahydrated solid solution begins to precipitate, and the invariant reaction at P is $L + 6\alpha + 6\beta \rightarrow 7 + \text{cals.}$ If the liquid is consumed, a 3-solid mixture is left. Otherwise, with 6α consumed the remaining liquid, dissolving 6β and precipitating 7, travels along Pp'_7 , or with 6β consumed it travels on Pp_7 , along which 6α changes to 7.

²⁴ Constructed from the study by A. Benrath and E. Neumann, *Z. anorg. Chem.*, **242**, 70 (1939).

Chapter XIII Discussion of Projections and Isotherms (of Chapter XII)

A. Methods of Determination

The practical representation of a ternary system, even simply at constant pressure, requires a suitable combination of projections, vertical sections, and representative isothermal sections, of the relations in the T/c prism. Each of these partial representations has its particular usefulness. Vertical sections, such as those of the systems of Fig. 12-16 shown in Fig. 12-21, are often the immediate result of thermal analysis carried out in the exploration of a series of such sections across the composition triangle. Each experimental section is then the plot of thermal breaks and halts, considered with respect to temperature and duration. The combination of a number of such sections, both parallel and intersecting, coupled with additional information based on visual, microscopic, or X-ray examination, is then interpreted from the point of view of schematic vertical sections of the possible phase diagrams likely to apply to the system. Guertler's *Klärkreuzverfahren* has been mentioned, as a preliminary aid to such investigation in systems containing binary and ternary compounds, as also the use of the intersection of straight-line crystallization paths for the determination of the composition of a primary crystallization product.¹ This last principle means that, with a sufficient number of such sections, it should be possible to identify all the phases of the system, stable at the melting point surfaces, and to work out their relations ("section method"). Once the curves and surfaces of crystallization are determined by sections, then the temperature (thermal break) at which a given complex reaches either such a surface or one of the curves of twofold saturation may be used to find the composition of the liquid phase at that point; the composition of the liquid and that of the total complex then determines a tie-line, which must also pass through the composition of the solid, a single phase or a mixture of two solid phases ("co-node methods").²

It is also possible to develop the phase diagram from the determination of a sufficient number of isothermal sections, coupled with the use of projections of curves of twofold saturation on the faces of the prism, to fix

¹ For application, see the papers by T. R. Briggs, mentioned in Chapter XII, Ref. 1.
² D. A. Petrov, *Acta Physico Chim. U.S.S.R.*, 14, 387, 497 (1941).

(through their intersections) the temperature and composition of the liquid at (isobaric) invariant points. This procedure, combined further with some thermal and dilatometric analysis, is frequently used for systems such as aqueous systems of salts, in which isothermal solubilities are easily determined, by separation and analysis of the saturated liquid phase. Ternary solubility isotherms may also be constructed without such separation and analysis, by the determination of some physical property of the solution as a function of the known total (synthetic) composition of the ternary complex. As pointed out under binary diagrams (Chapter IX-A), the liquid properties will vary continuously as long as the liquid is unsaturated, and a break will occur upon saturation with any phase, after which the rate of change of the property is again continuous. When the system reaches a 3-phase (condensed) equilibrium state all the properties of the liquid are isothermally invariant. In this way the electrical conductivity³ or the refractive index,⁴ for example, of the liquid phase may be used for the plotting of ternary solubility isotherms.

B. Projections

1. Polythermal Projection

This type of projection, discussed in Chapter XII (Fig. 12-18, for example) is used to follow the course of events on cooling liquids of known composition, in respect to the thermal behavior (breaks and halts) and to the significance of these breaks in terms of the solid phases appearing and disappearing. Through the projection the relative amounts of the phases at any particular point in the process may be calculated, once a curve of twofold saturation is reached. Calculations (approximate) on the crystallization surfaces (for saturation with a single solid) require temperature contours, which may be considered part of the polythermal projection, as a superposition of a number of isotherms on one plane.

Chapter XII discussed particularly the process of solidification with complete equilibrium between liquid and solid phases. It was also pointed out that the path followed by a liquid, and hence its thermal behavior, is not always that of complete equilibrium if the solids are not given time to adjust their composition or to redissolve as demanded by the complete equilibrium relations. If all the curves of twofold saturation are curves of positive crystallization of both the solids involved, as in Figs. 12-18, 12-25, 12-28, the crystallization paths for "effective removal" of solid are those already shown on those figures for full equilibrium, provided that the solids are pure. When the system $L + X$ (that is, liquid precipitating a pure solid

³ H. A. Taylor and N. R. Trenner, *J. Phys. Chem.*, **35**, 1336 (1931).

⁴ K. I. Mochalov, *J. Gen. Chem. U.S.S.R.*, **9**, 1701 (1939).

X during cooling) reaches a curve on which the reaction is $L, X+, Y+$, the liquid travels along that curve to an invariant point, whether the original X is present or removed; these curves are not crossed in such cooling. On the other hand, when the system $L + X$ reaches an "odd" curve, on which the reaction is $L, X-, Y+$, and X is not given time to dissolve (or if X is removed, as by filtration), the liquid composition does not stop on the curve at all (although there will be a break in the cooling curve) but crosses it, changing only its direction while Y is being precipitated (and added to X if this is still present). The arrows representing direction of falling T on these curves therefore have no significance for such non-equilibrium solidification, since only even $(++)$ curves are then traveled.

As for invariant points, only those are reached, during solidification with "effective removal of solid," which have at least one such even $(++)$ curve leading to them with falling T . But the temperature is held constant only at a eutectic point. Peritectic points, if reached, merely mark a change in direction for the liquid composition, with a break in the cooling curve, even when, in equilibrium solidification, they would be incongruent crystallization end-points. Thus point P of Fig. 12-25(b) is reached by two even $(++)$ curves, but if solid C is not given time to dissolve when the liquid reaches P, the liquid moves immediately to the curve PE, precipitating more D and A, and ends at the crystallization end-point E, leaving a mixture of four solids.

2. Perspective T/c Projection⁵

A perspective projection on the CB face is one which shows the proportions of the components C and B on all the ternary curves of twofold saturation but does not represent the concentration of A. The simple system of Fig. 13-1 appears in three such projections in Fig. 13-2. The temperature at which the liquid P begins to precipitate B may be determined from a vertical section of the T/c prism through BP, but also approximately from a polythermal projection such as Fig. 13-1 if this contains a sufficient number of contours of constant T . The temperature at which the secondary crystallization starts (of C with B) when the liquid reaches point x on the curve e_2E may be clearly obtained, however, from the combination of projections (Figs. 13-1 and 13-2) since the composition x , fixed by the line BPx in

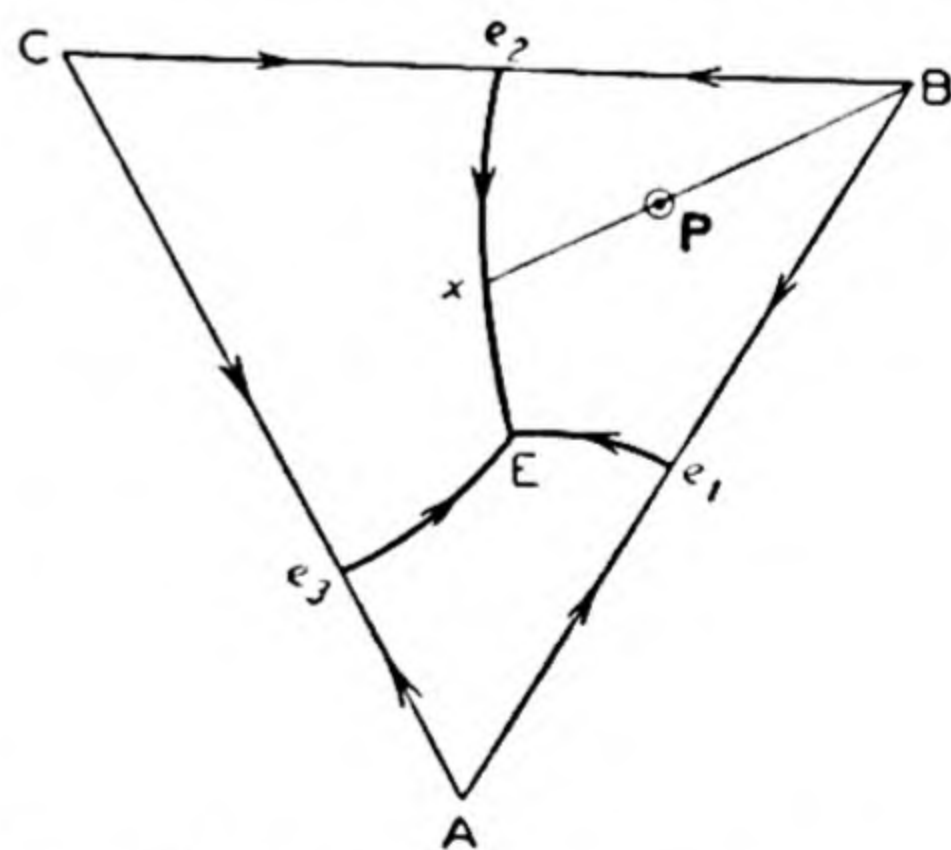


FIG. 13-1. Polythermal projection of simple system.

⁵ E. Jänecke, *Z. anorg. Chem.*, **51**, 132 (1906).

Fig. 13-1, may then be used on any of the three projections to read the temperature on the curve e_2E , through the use of the proportions of B and C at the point x , in 13-2(a), of B and A in 13-2(b) or of A and C in 13-2(c).

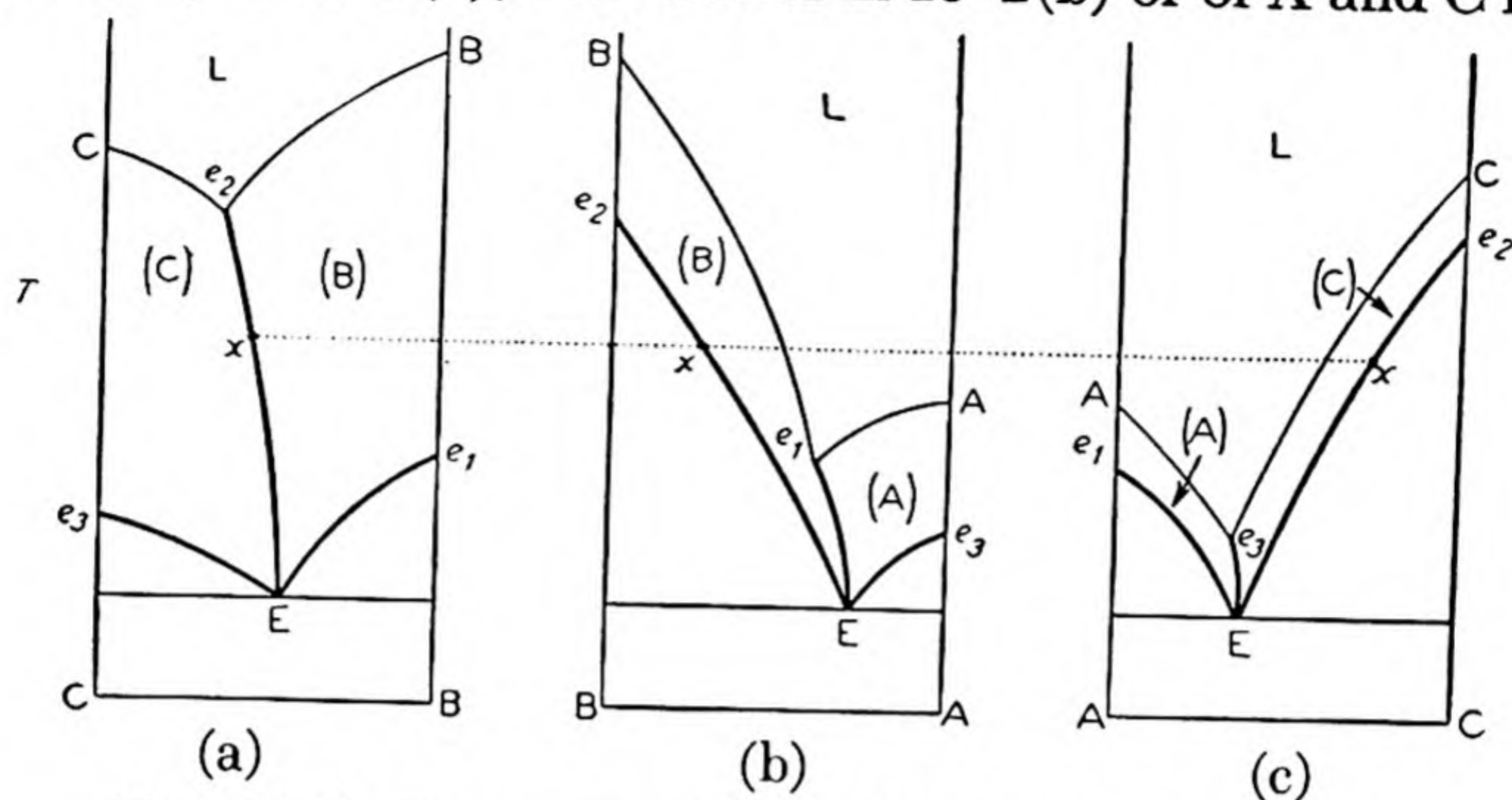


FIG. 13-2. Perspective T/c projections of Fig. 13-1.

Fig. 13-4 shows similar perspective projections for a system with a binary compound, D, of the components C and B (Fig. 13-3). The temperature of any point on one of the curves of Fig. 13-3 may be found from any one of the projections. The composition for any temperature on one of the curves is found by the use of two projections simultaneously. Thus the composition of a solution at T_x , on curve mE_1 , saturated with D and A, may be

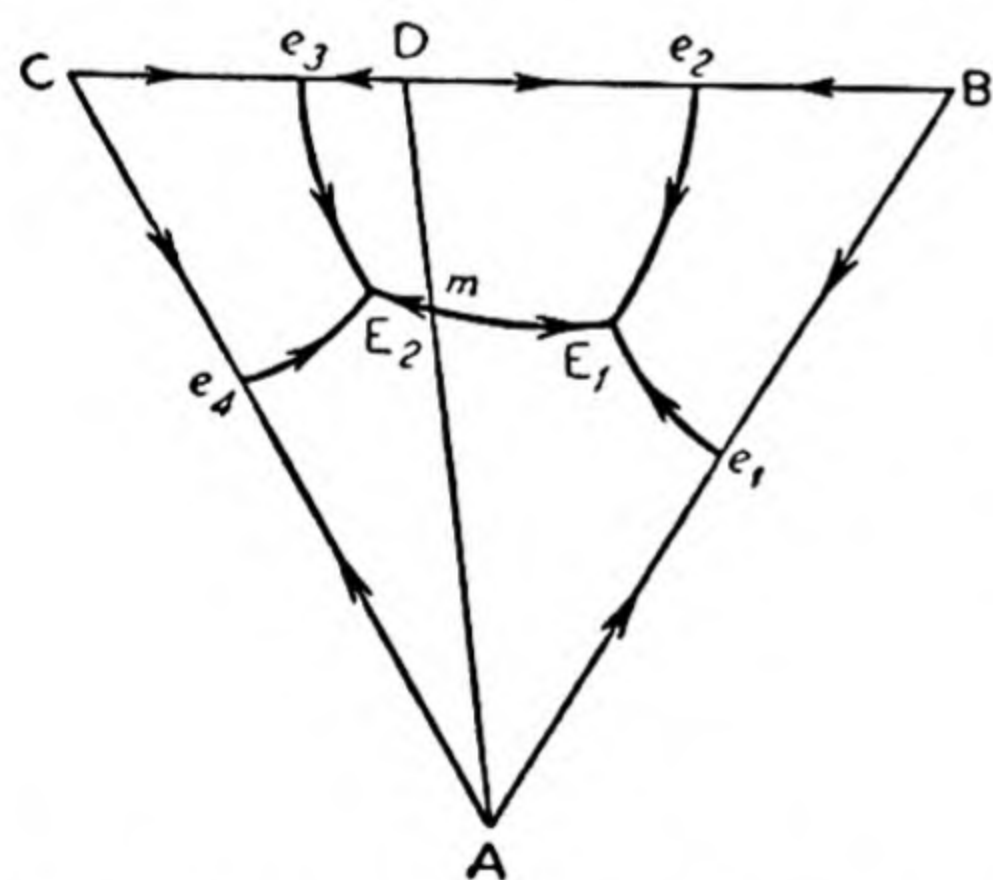


FIG. 13-3. Congruently melting binary compound; polythermal projection.

read from Fig. 13-4(a) for the C/B ratio and from 13-4(b) for the B/A ratio, whereby the ternary composition may be obtained. In Fig. 13-5, a system with two binary compounds is shown in perspective projection on the CB face. It is clear that any one of the projections may be used for the determination of transition temperatures, such as P of Fig. 13-5, through the intersection of the projected curves; with two projections, the complete composition of the invariant liquid may also be determined.

In these perspective T/c projections, the compositions are plotted in terms of proportions of two of the components, the third being ignored, so that they are not necessarily the vertical sides of a T/c prism with an equilateral triangle as the composition plane. Fig. 13-4(a) simply plots percentage of B in B + C.

3. Special Diagrams

When one of the components, such as water in the system NaCl-KCl- H_2O , plays a rather special role in the ternary system, the composition

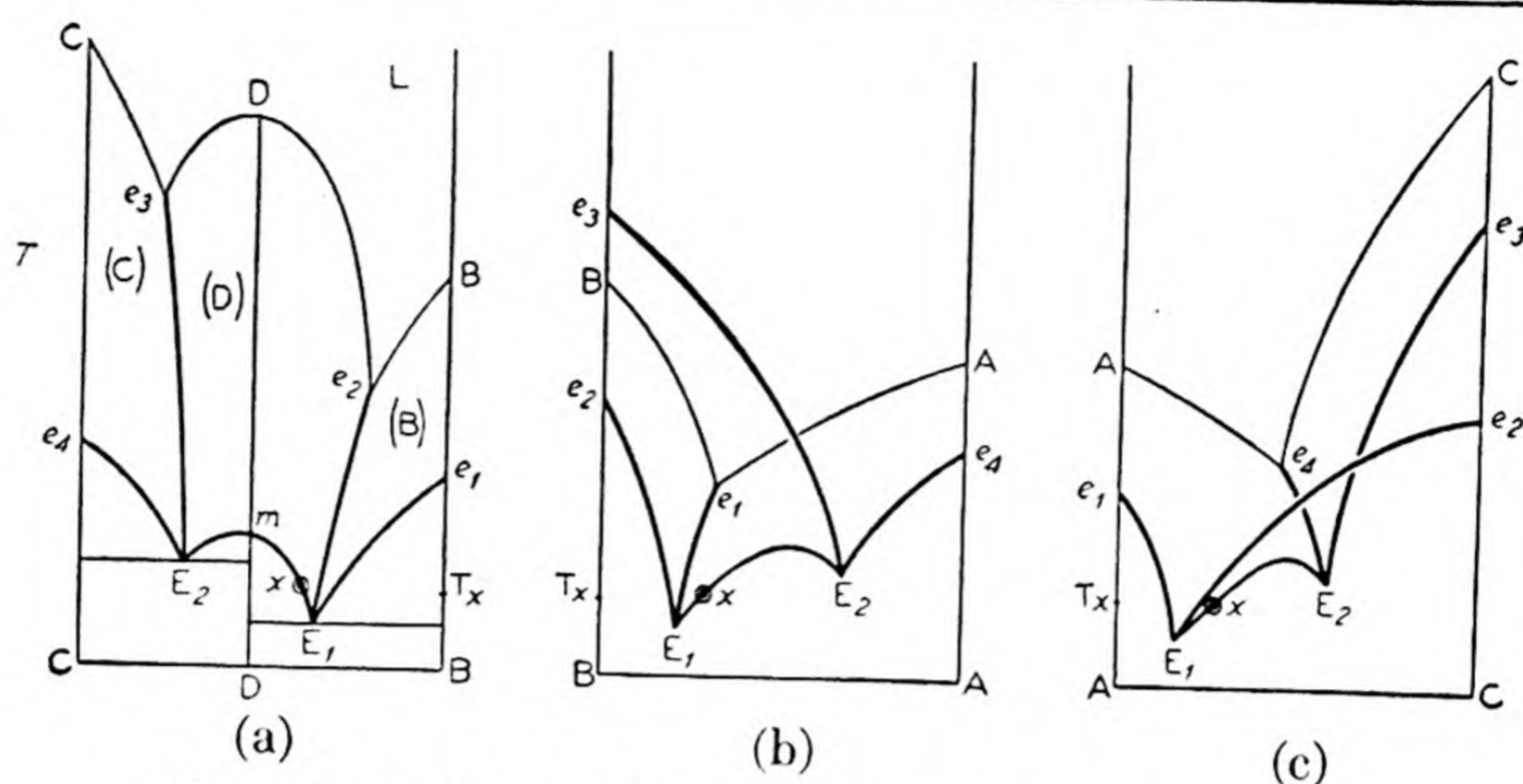
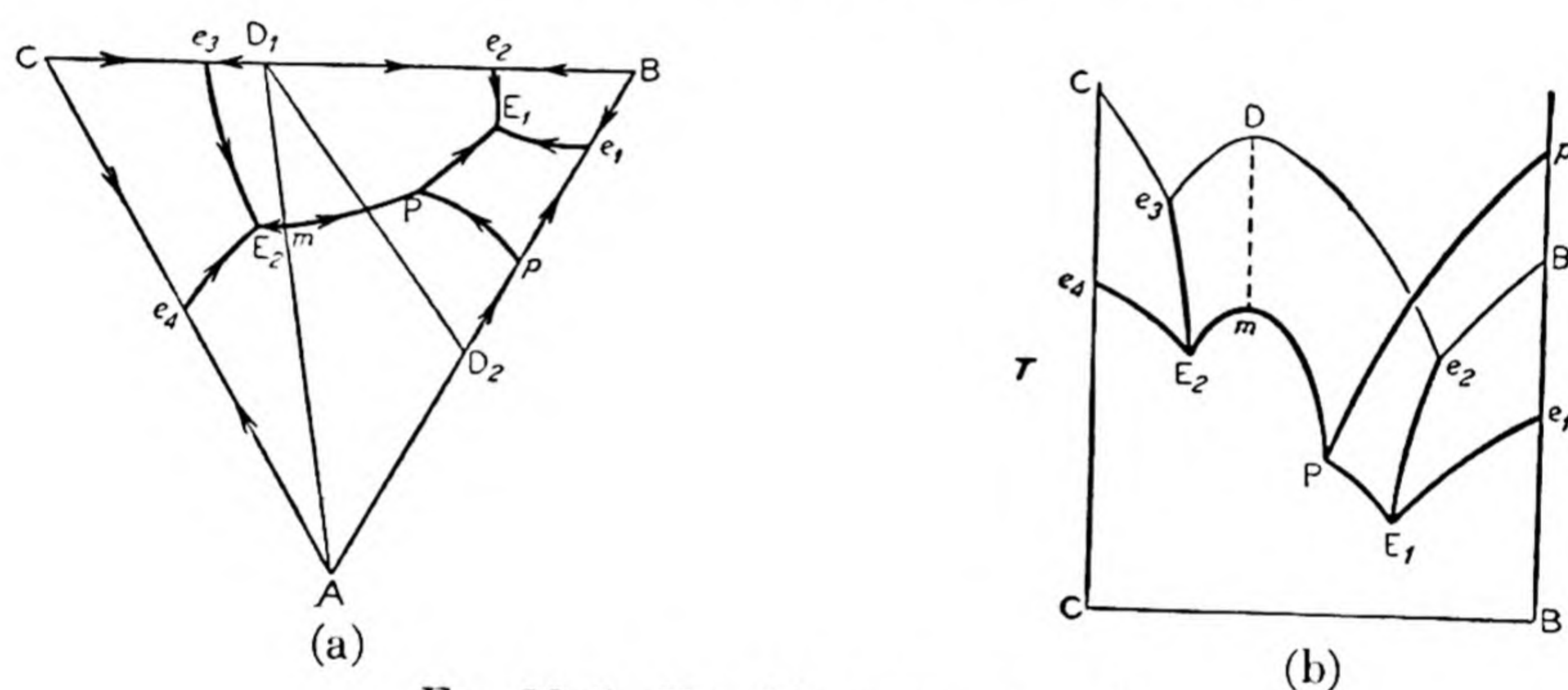
FIG. 13-4. Perspective T/c projections of Fig. 13-3.

FIG. 13-5. Two binary compounds.

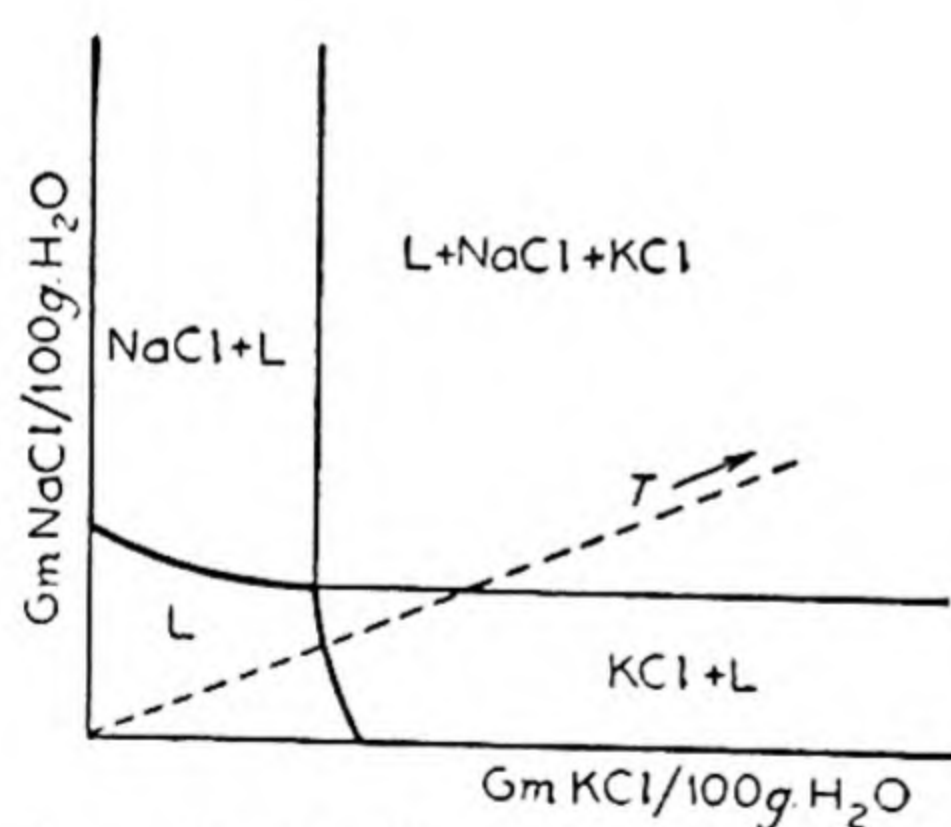


FIG. 13-6. Rectangular coordinates representing ratios.

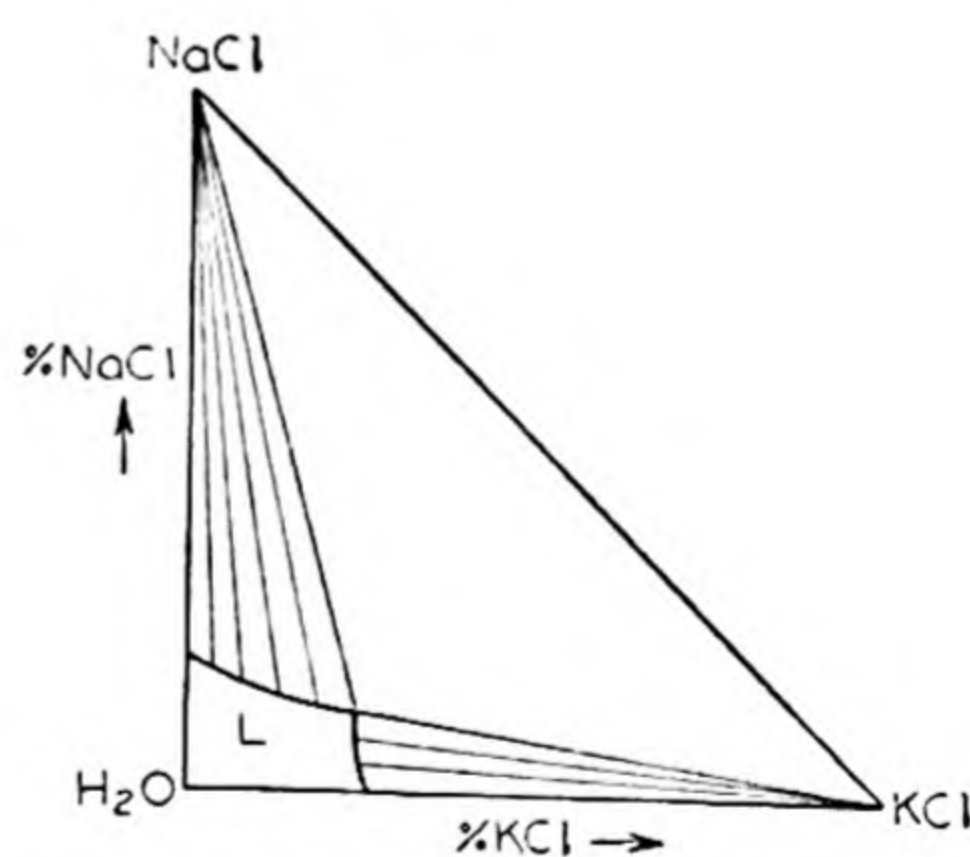


FIG. 13-7. Isosceles right triangle as composition plane.

plane is often, for special convenience, given special forms. The quantity of each salt per unit quantity of water (grams or moles) may be plotted on one of two axes intersecting at 90° , as in Fig. 13-6, with T as an axis perpendicular to the concentration plane, as shown in perspective in the figure. The concentration axes are here infinite in length, and the pure salts cannot be

P is the ternary peritectic point ($L, NaCl-, NaCl \cdot 2H_2O +, KCl+$), and E is the ternary eutectic. In the projection (Fig. 13-9) the fields overlap, the KCl field lying on part of the ice field in the NaCl-H₂O projection, and the NaCl \cdot 2H₂O field lying on part of the ice field in the KCl-H₂O projection. But these projections, together, give the concentrations and temperatures along all the ternary curves.

The polythermal projection for Fig. 13-8, but based on the isosceles triangle of Fig. 13-7 as composition plane, is Fig. 13-10 (schematic). The

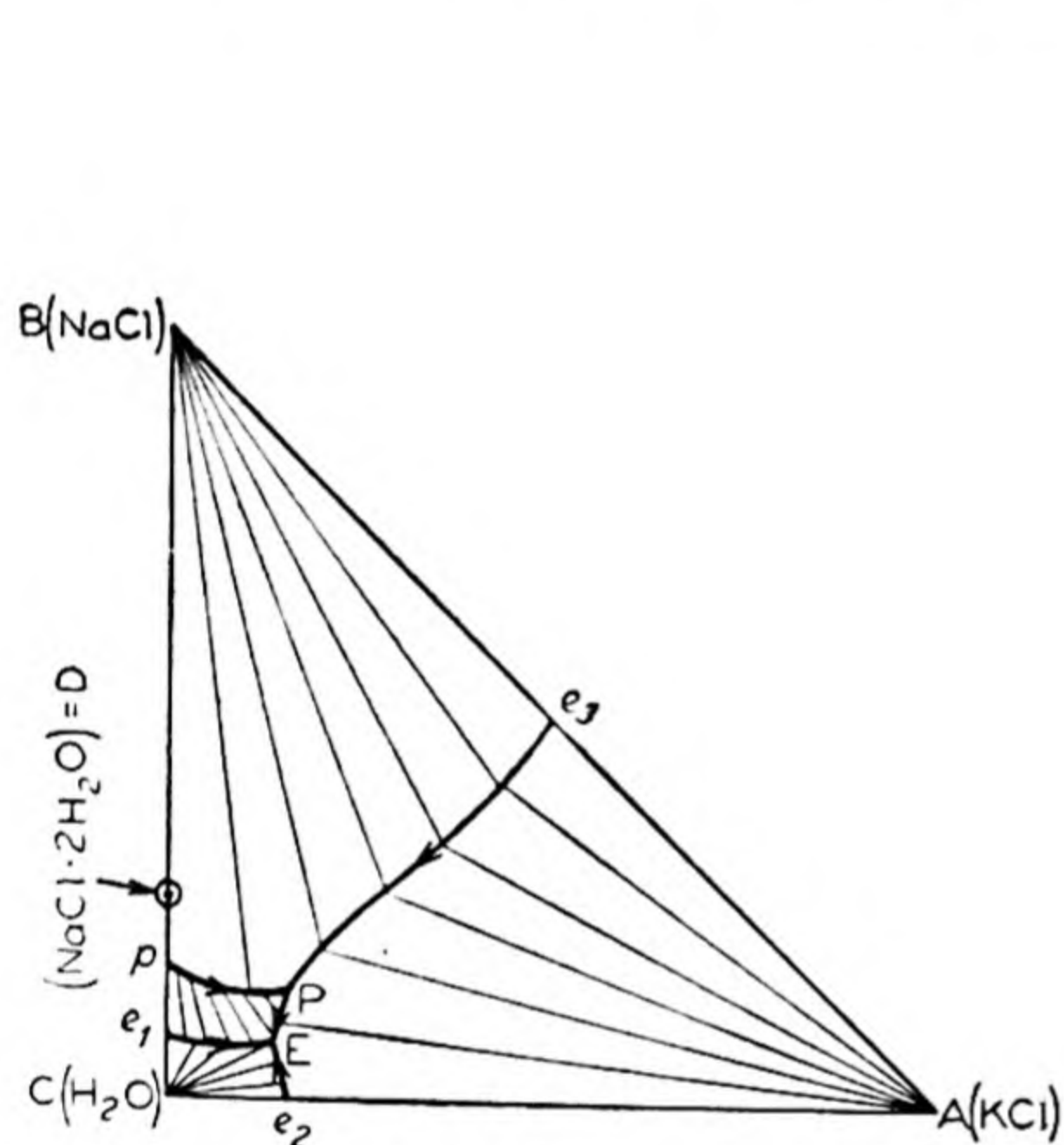


FIG. 13-10. Polythermal projection (schematic) of system NaCl-KCl-H₂O.

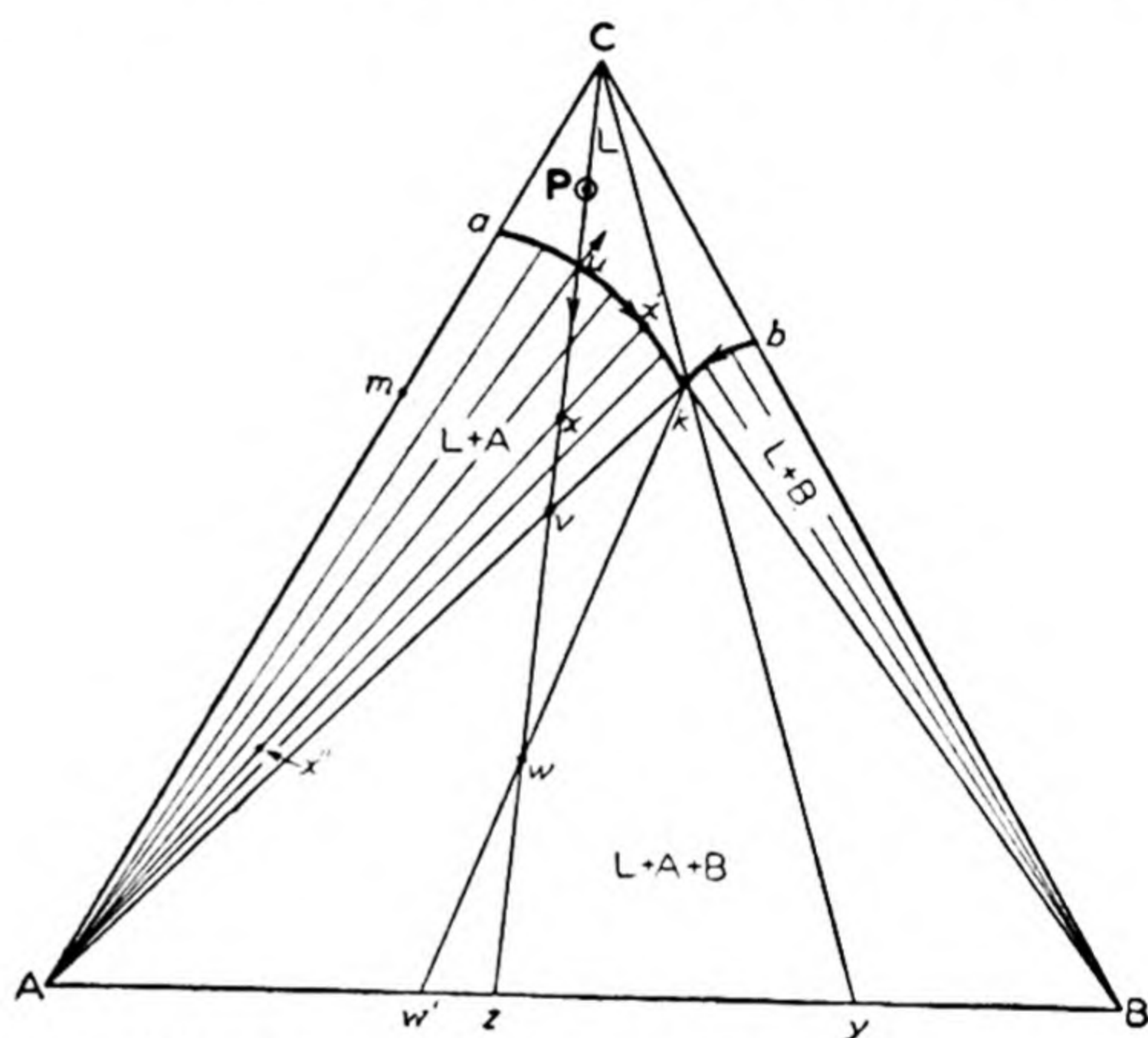


FIG. 13-11. Schematic isotherm for two pure solids and one liquid.

ternary peritectic point is seen to be the incongruent crystallization end-point for liquids with original compositions in the triangle ABD. The temperatures are $+0.15^\circ$ for p , -21.85° for e_1 , -11.1° for e_2 , -2.35° for P, and -23.7° for E.

C. Isotherms (Condensed Systems)

1. Simple case: Solvent (C) + Two Solid Components (Fig. 13-11)

Point a is the solubility, measured from C to a , of solid A in liquid C; the line aC is homogeneous binary solution, while a mixture, m , of A and C gives at equilibrium the saturated solution a and excess of solid A, the proportions being $a/A = Am/ma$. The curve ak is called the solubility curve of A in the ternary liquid, as affected by the concentration of B. Whether the solubility of A may be said to fall or rise from a to k depends on the definition of solubility, which may mean any one of the ratios A to C, A to B + C, or A to A + B + C, and on the units in which the diagram is plotted. With the assumption of certain ideal relations, the two

solubility curves may be calculated in some cases, even up to their intersection k , which is the (condensed, or isobaric) isothermally invariant solution saturated with both solids. If A and B are two salts with common ion, the initial effect of one salt, B, upon the solubility of the other, A, will generally be to decrease it; with complex ion formation the solubility of A may pass through a minimum upon addition of B, or may even be increased from the start.

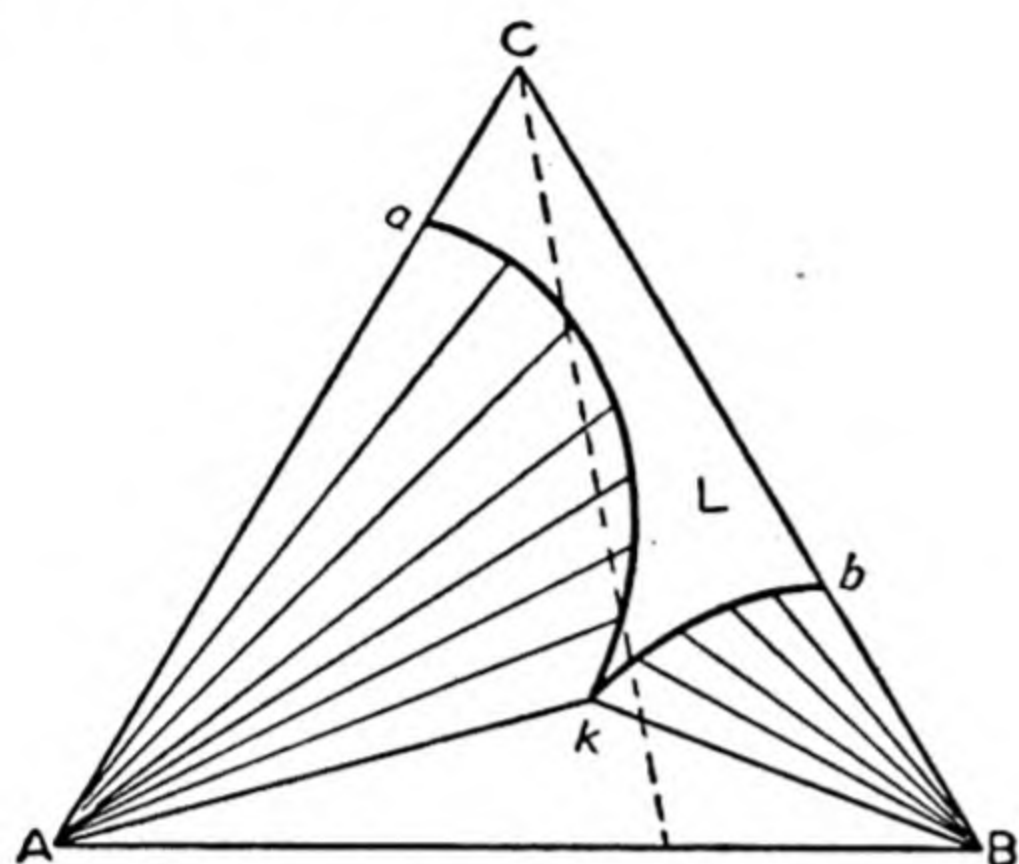


FIG. 13-12. Variation of
Fig. 13-11.

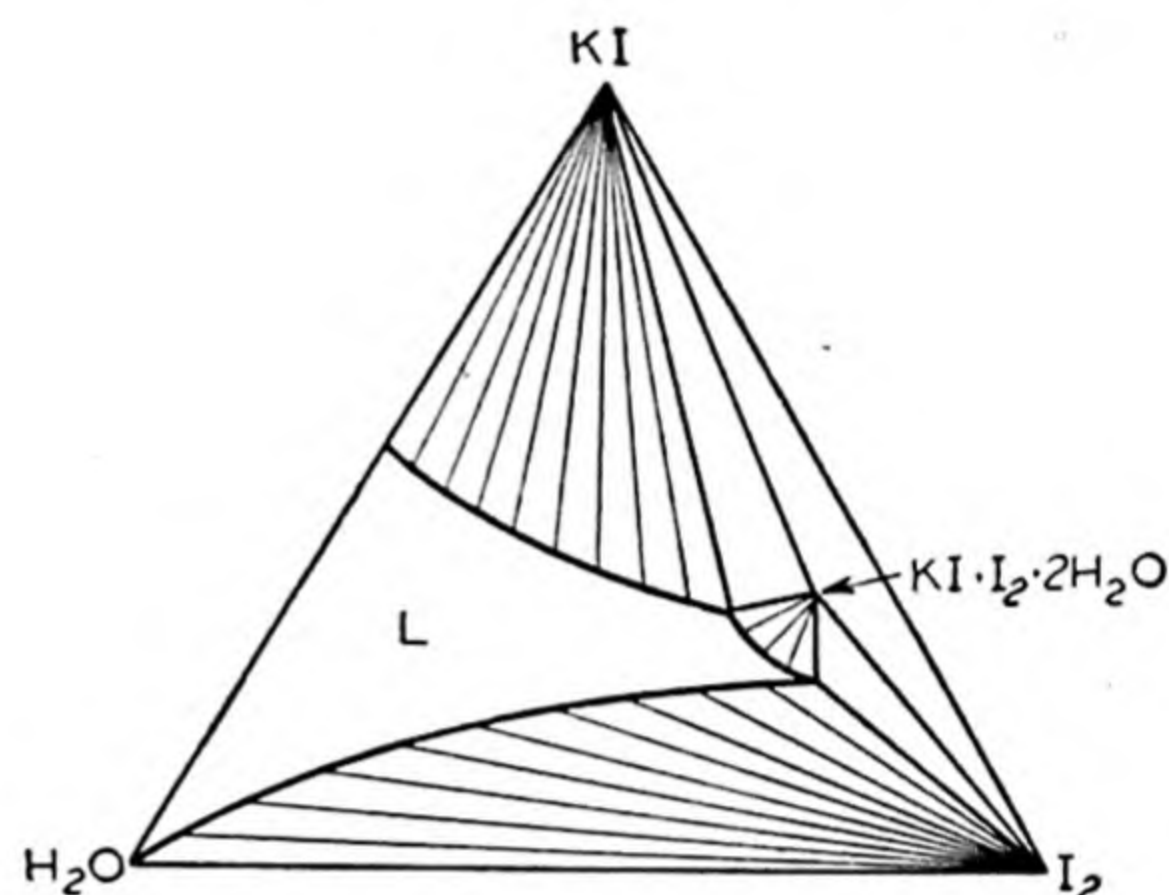


FIG. 13-13. Isotherm at 0°C
for system I_2 -KI- H_2O .

In any case, the two solubility curves will intersect in one of the two ways given in Fig. 11-27(a and b); and as the temperature rises to approach the eutectic of the system A-B, the curves must come to intersect as in Fig. 11-27(a). Abnormal increases in the solubility of one of the components result, of course, from the formation of complex species in the solution, whether or not solid compounds actually appear. Fig. 13-12, with a "retrograde" effect of B on the solubility of A, would be the analog of Fig. 5-2(b). In the isothermal relations of the system I_2 -KI- H_2O , shown schematically in Fig. 13-13 for the temperature 0°C, we see the effect of the formation of the complex triiodide anion on the solubility of iodine.⁶

The region marked L, then (in Fig. 13-11), is that of unsaturated ternary liquid phase; compositions in the tie-line areas give a saturated liquid solution, on the solubility curve, and excess solid; and compositions in the isothermally invariant triangle, AkB , give liquid k and two solids. In a 2-phase region, the composition x consists, at equilibrium, of liquid x' and solid A in the ratio xA/xx' . In the 3-phase region, the composition w consists of liquid k and the solid mixture w' in the ratio ww'/kw , the solid mixture containing A and B in the ratio Bw'/Aw' .

Finally, if A is a pure solid, the activity of the solvent C in the saturated solution falls from a to k on the solubility curve of A. In an aqueous system,

⁶ T. R. Briggs, K. D. G. Clack, K. H. Ballard and W. A. Sassaman, *J. Phys. Chem.*, **44**, 350 (1940).

then, in which A and B are non-volatile solids and C is water, the vapor pressure of the saturated solutions falls from points a and b to a minimum at k . In general this means that the water concentration of the saturated liquid solution, or W_l , will usually also decrease from a and b to a minimum value at k . In aqueous salt systems a curve such as ak may show a maximum of water content in terms of weight percentage between a and k , but we may expect that in practically every case the analytical mole fraction of water will fall continuously from a to k , which will then normally be a point of minimum water content. Strictly, even this may not hold, for it is the activity and not the concentration of the solvent that must fall from a to k for saturation with pure solid A. We shall, for brevity, use the term "water content" or the symbol " W_l " to mean strictly the aqueous vapor pressure of such a system, but normally the concentration of the water, such as its analytical mole fraction, in the solution.

a. *Indirect analysis of solid phase.* The tie-lines in a 2-phase region involving a pure solid phase converge at the composition of the solid (the corners A and B, in the present case), a fact, as already pointed out, which can be used to identify solids and determine their composition. In Schreinemakers's "method of wet residues" ⁷ a tie-line is determined by analyzing the saturated solution (x') and also a sample of the solid phase still wet with the mother liquor. This wet residue must be a point, such as x'' , fixing a line joining the liquid and the solid phase. It is also possible to make up a ternary mixture of known composition (a known, synthetic total complex) such as point x , and then to fix the tie-line by analysis of the saturated solution at equilibrium.⁸ In either case, graphical or algebraic extrapolation of the set of tie-lines to their point of intersection determines the composition of the solid without the necessity of its separation from mother liquor and of its drying preparatory to chemical analysis. If the tie-lines intersect with precision at the point supposedly representing a definite solid, the solid phase may be assumed to be pure, forming no solid solution with adjacent solid phases. If the tie-lines fail to intersect sharply, but show some regular trend beyond experimental error, indicating an increasing proportion of B in "solid A," for example, as the concentration of B in the liquid increases from a to k , then it may be inferred that A is taking up B in solid solution.

As a consequence it may be easier to determine isothermal binary relations by studying them as part of a ternary system than by the study of the binary system alone. The question whether two solids at room temperature, far below their melting points, react in any way to form either compounds

⁷ F. A. H. Schreinemakers, *Z. phys. Chem.*, **11**, 75 (1893).

⁸ A. E. Hill and J. E. Ricci, *J. Am. Chem. Soc.*, **53**, 4305 (1931).

or solid solution may be answered through the study of their ternary system with water (or other suitable solvent), provided that the solid phases are anhydrous, for then the base of the isothermal diagram is the binary system of the solids, the behavior of which is revealed by the tie-lines from the solubility curves.⁹ Similarly the composition of a hydrate (a binary compound) may often be determined more easily and accurately from a ternary isotherm involving a soluble third component (such as a salt or an acid) than by direct chemical analysis in the binary system itself. If the A phase in Fig. 13-11 were hydrated, for example, all the tie-lines on the curve *ak* would converge at the composition of the hydrate; and it is clear that if the component B is very soluble, the curve *ak* will be long and the tie-lines from the *k* end of the curve may determine the hydrate composition rather accurately, if the solid phase remains the same along the curve.

A frequent difficulty in the direct separation and analysis of a saturating solid phase is the problem of the correction for the quantity of mother liquor contaminating it. Essentially the component B is being used as a "tracer," in Fig. 13-11, for this correction, since this is the effect of the extrapolation of the tie-lines to their intersection with the side AC to determine the hydration of the A phase. The "tracer method" may be extended for the identification of compounds other than simple hydrates. One adds a known small amount of a foreign fourth component in a ternary system¹⁰ (or a fifth in a quaternary system, etc.) which must be liquid-soluble and solid-insoluble, causing no change in the nature of the heterogeneous equilibria under investigation. If it is possible to determine with sufficient accuracy the concentration of this substance, at equilibrium, both in the mother liquor and in the wet solid, then the correction for mother liquor may be made.

If A and B are non-volatile, with C easily vaporized and determined, and if a solid phase is known not to contain C in its composition, then the correction for mother liquor may be made easily by determining the C content of the wet solid. This applies for an anhydrous solid phase in an aqueous system involving non-volatile salts. If the solid phase is hydrated, this procedure may still be followed, but with modification. In order that the quantity of mother liquor in the wet solid may be determined, for the purpose of correcting its analysis, the water of the contaminating solution must be evaporated not by heating but by using a desiccator containing

⁹ Examples are mentioned in Chapter VI: reference 2 under Fig. 6-3(a) and reference 5 under Fig. 6-5(d). On the use of vapor pressures of aqueous solutions saturated with two salts for the determination of certain points of the binary system of the two salts, see A. E. Korvezee, P. Dingemans and L. L. Dijkgraaf, *Rec. trav. chim. Pays-Bas*, 66, 383 (1947).

¹⁰ A. van Bijlert, *Z. phys. Chem.*, 8, 343 (1891).

as the hygostat a system with a vapor pressure not smaller than the decomposition pressure of the hydrated solid phase itself. Since this is an unknown pressure if the solid phase itself is still unknown, it is sometimes possible to use as the hygostat another sample of the phase itself, already partially dehydrated by exposure to dry air or to a vacuum.¹¹

Finally, it is also possible to identify a solid phase¹² by analyzing the saturated liquid, adding some of the suspected solid, shaking again to establish equilibrium, and reanalyzing the liquid. If the solid added is a saturating phase already present, there will be no change in the composition of the liquid. This "zero method" applies for any degree of complexity of the liquid and for any number of saturating phases, since the addition of excess of any or all of the saturating solids cannot affect the composition of the liquid.

b. *Isothermal evaporation and dilution.* If C is water and A and B are non-volatile solids, then the isothermal evaporation of an unsaturated solution of composition **P** (Fig. 13-11) causes the composition of the liquid to move away from the corner C, on the straight line through C and **P**. The solution remains unsaturated until the composition reaches the point *u*, on the solubility curve of A. As A is precipitated the composition of the liquid travels along the curve toward *k*, while the total composition (of the condensed phases, solid and liquid) always lies on the line **CPz**. When, through loss of water, the total composition reaches *v*, the liquid will have reached *k*, and at this point the liquid begins to precipitate a mixture of A and B, in the proportions in which they are present in *k*, or $A/B = y_B/A_y$, if the line Cy passes through *k*. As the evaporation is continued, the total solid composition approaches *z*, and the last trace of liquid to dry up still has the composition *k*. The process leaves a mixture of A and B represented by point *z*.

Similarly, if liquid C is added to the mixture *z* of A and B (isothermal dilution), the composition follows the line Cz toward C, and the phenomena just described are reversed. A solution of constant composition *k* is immediately formed, and as point *v* is approached, the proportion of B in the solid mixture is diminishing, since A and B are dissolving together in the proportions given by the point *y*. When enough C has been added to give the total composition *v*, B is all dissolved, and the liquid, now saturated with A alone, travels along the curve *ak* toward *a*. When the total composition reaches *u*, A will also have been dissolved, and the liquid becomes unsaturated, entering the L area.

The relations for isothermal evaporation may be summarized in such a

¹¹ A. E. Hill, *J. Am. Chem. Soc.*, **52**, 3817 (1930).

¹² W. D. Bancroft, *J. Phys. Chem.*, **6**, 179 (1906).

diagram by direction arrows on the solubility curves. These arrows indicate the course followed by the composition of a saturated liquid during isothermal evaporation of the solvent. The direction on the curve ak must be that shown, because of the vectors (drawn at point u , for example) for the simultaneous removal of C (by evaporation) and of A (by precipitation) from the liquid. Similarly, therefore, evaporation of the saturated solution on the curve bk is accompanied by precipitation of B, and hence point k is the isothermal **drying-up point** for the system (the W_l minimum).

c. "*Water content*" as the variable in isothermal evaporation. If the system of Fig. 13-11 is plotted according to the method of Jänecke, with the water content W_l as the ordinate, and proportions of the non-volatile salts A and B as abscissa, we have Fig. 13-14. The process of isothermal evaporation or dilution of the ternary liquid is that of decreasing or increasing its aqueous vapor pressure (" W_l ," as defined above in contrast to W_t , the total water content of the condensed phases, liquid + solids). Such a process for a ternary system at constant T is seen to be closely analogous

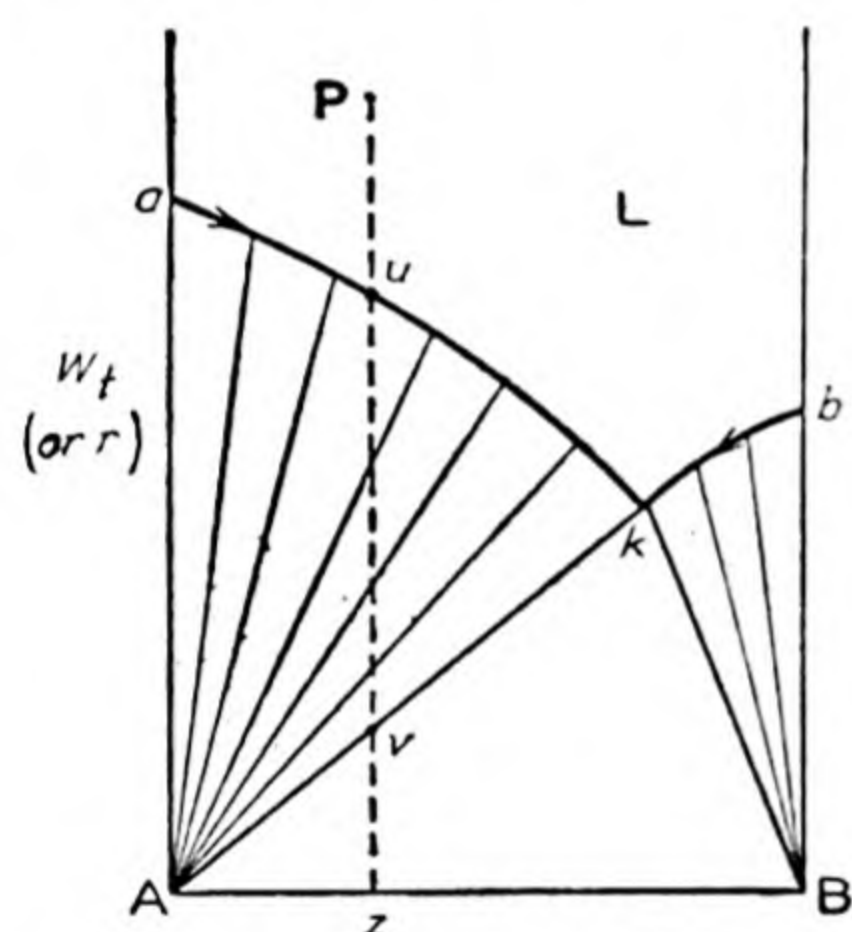


FIG. 13-14. Jänecke diagram for the isotherm of Fig. 13-11.

to the variation of temperature for a binary liquid at constant pressure. With respect to W_l , the water content (strictly vapor pressure) of the solution, the present simple system behaves as a simple eutectic binary system behaves with respect to T in the process of solidification or melting. Decreasing W_l for an unsaturated solution of pure A leads to an (isothermally) invariant halt at a , with $W_l = a$. If W_l is decreased upon the solution P, there will be a break in the curve of W_l plotted against the total water content W_t (or, if preferred, the ratio, r , of solvent to salts in the total system), when the curve ak is reached at point u , and finally an invariant

point at k when $W_l = W_k$. A solution of composition k dries up invariantly, at $W_l = W_k$, just as the binary eutectic liquid solidifies invariantly on cooling.

The points a , u , k are points of initial isothermal crystallization for the three compositions a , u , k respectively, and they give the value of W_l for the beginning of crystallization. For pure A, the value of W_l during crystallization is constant and independent of the total water content of the system or of the ratio r (and hence also of what may be called the "fraction dissolved"); the same is true for solution k . But in the region between a and k , the value of W_l for the start of crystallization depends on the proportions of A and B, and it then varies, during crystallization, with r (and hence

also with the "fraction dissolved"). Expressed differently, the "total solubility" or the total concentration ($1-W_l$) of the saturated solution is independent of r for pure A (and for k) but is a function both of the proportions of A and B and of the ratio r , for all other compositions.

For the isobaric freezing and melting of a binary system, the analog is T for W_l , and fraction melted for fraction dissolved, respectively. In the binary system the eutectic mixture may be distinguished from a pure component by changing the pressure, whereupon its melting point becomes a function of the fraction melted. Similarly the mixture of A and B in the proportion k may be distinguished from a pure component by measuring the solubility at a different T , whereupon the concentration of the saturated solution becomes a function of r or of the fraction dissolved.

d. *Purification of a solid.* If the mixture z , of Fig. 13-11, is treated with a limited amount of the solvent, there is an immediate enrichment of A in the residual solid, for as the total composition moves on the line zC toward v , the composition of the mixed solids moves on the line AB toward A. This follows since, as explained above, the liquid first formed has the fixed composition k , and the tie-line joining k and the mixed solids must pass through the total composition, which is rising on the line zv . If this liquid is poured off, a purer sample of A is left. The yield can be calculated from the proportion of solvent (r) used; the smaller the yield, the higher the purity of the residue. If enough solvent is added to enter the field Aak , then pure A may be obtained; the maximum yield of pure A would result from the use of just enough solvent to enter this field. This may be called purification by seeping. In purification by recrystallization, the sample is first completely dissolved, usually at a higher temperature where the solubility is higher, and the solution is then evaporated and crystallized at the lower T . If the evaporation is not carried beyond the point v , pure A is deposited. If an impure sample of B (the more soluble solid) is to be purified by these methods at the temperature of the isotherm of Fig. 13-11, no enrichment is possible unless the mixture is already richer in B than the point y , on the line Cky , and the yield will always be relatively low.

e. *Separation of a mixture by a temperature cycle of crystallization.* Fig. 13-15 (schematic) is the superposition of two isotherms of the system NaCl-KCl-H₂O. The 0° isotherm is partly metastable, the curve kb being the solubility curve of anhydrous NaCl; the stable phase at this temperature is the dihydrate (transition point + 0.15°), which, however, does not readily form, so that the metastable is the significant curve. The point m is an unsaturated solution of a 1:1 mixture of the salts. If it is evaporated at 100°, it begins to precipitate NaCl when it is concentrated to the point x on the curve $k'b'$. As NaCl is precipitated, the solution travels on this

curve toward k' . If the evaporation is stopped just as the liquid reaches k' , pure NaCl may be filtered off, at 100° , leaving a liquid of composition k' . If this is cooled to 0° , it lies in the field KCl- a - k for the equilibrium KCl + liquid at 0° , and it therefore separates into KCl and a liquid of composition y , on the curve ak . The KCl is filtered off and the liquid y is mixed with more of the original solution m , to give a liquid of composition y lying on the line my , such as m' . If this solution is now subjected to the same cycle of operations, it is clear that after separation of NaCl at 100°

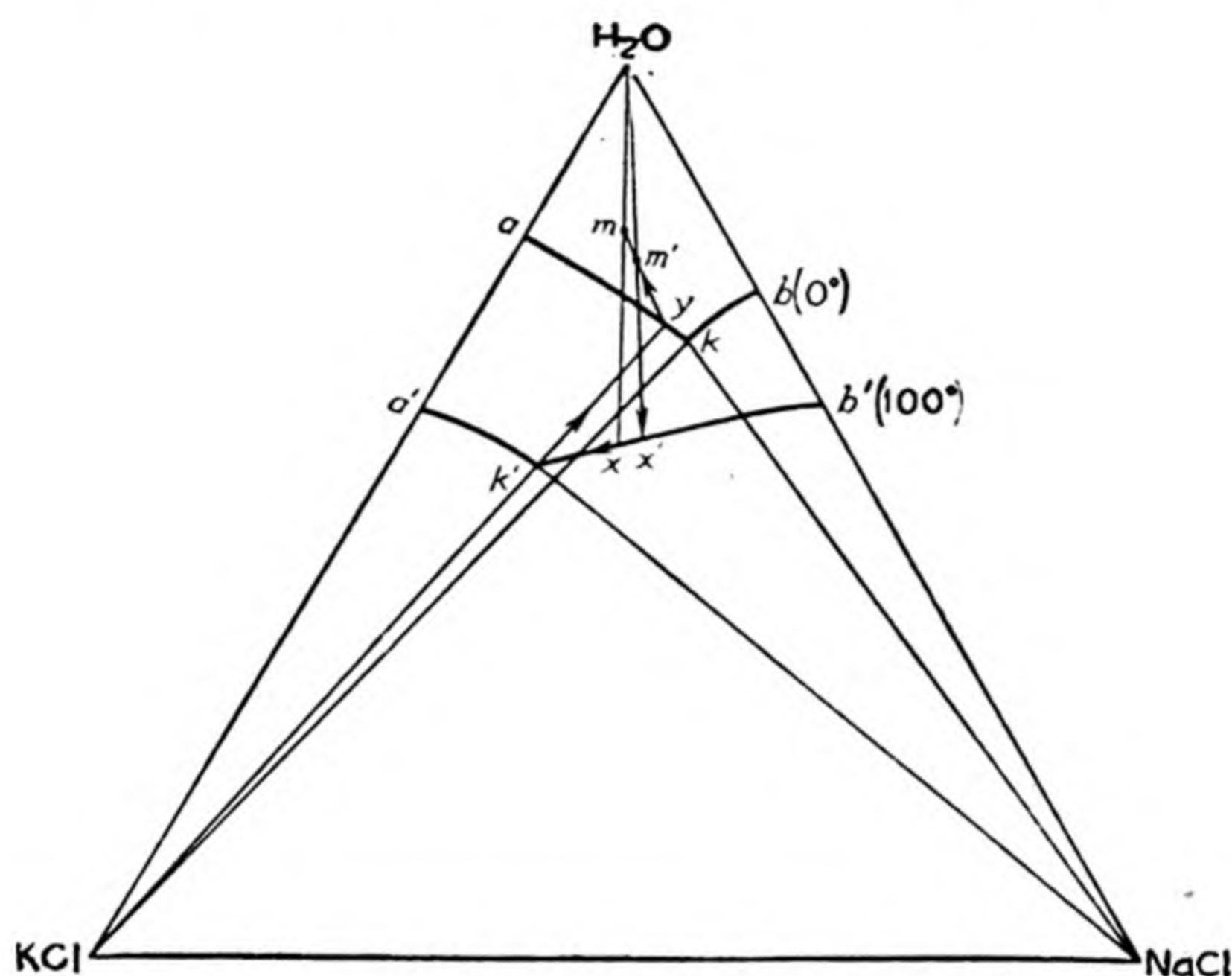


FIG. 13-15. Separation of a mixture by crystallization cycle.

and of KCl at 0° , a solution of composition y is again obtained. This solution is called the "nucleus solution" of the process and forms the starting point for each crystallization cycle. The quantities of the salts recovered in each cycle, and the extent to which the evaporation must be carried at 100° , may be calculated through simple algebraic relations if the compositions of the points m , y , m' (m' calculated from the proportions of m and y taken at the start of the cycle), x' , k' are all known.

The process¹³ depends on the fact that the points k and k' have different ratios of the salts. To begin with, if these ratios were the same as at m , neither salt could be obtained pure. If k' should fall inside the triangle KCl- k -NaCl at 0° , but still to the left of mx , pure NaCl could be obtained by evaporation at 100° , but only impure KCl would be produced by crystallization at 0° . This is the situation for KCl- K_2SO_4 - H_2O ,¹³ between 0° and 100° . One salt may always be obtained, pure, by isothermal evaporation at the higher T , if k' and m do not have the same salt ratio; but the second

¹³ W. C. Blasdale, *J. Ind. Eng. Chem.*, **10**, 344 (1918).

salt can be obtained, by crystallization at the lower T , only if k' lies in the isothermally univariant field of the salt at the lower T .

2. Hydrates

Fig. 13-16(a) shows one hydrate for B (B_1) and a lower and higher hydrate for A (A_1 and A_2). At the temperature of the isotherm the saturated solution in the system H_2O -B is in equilibrium with the hydrate B_1 , its solubility being e . As A is added to the system, this solubility follows

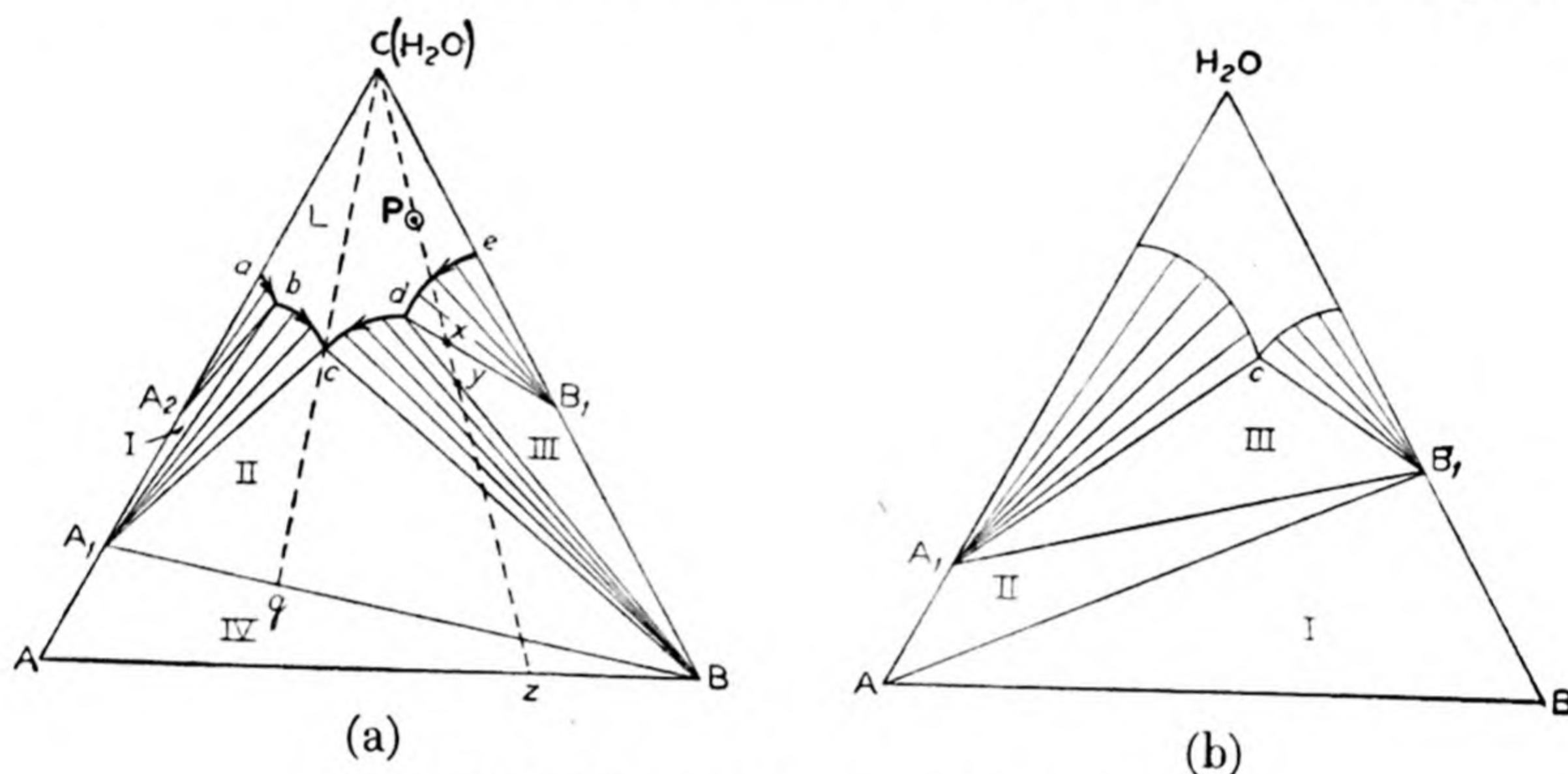


FIG. 13-16. Schematic isotherm with hydrates.

the curve ed ; at d the vapor pressure of the solution has been lowered sufficiently so that anhydrous B becomes the stable saturating phase, and its solubility curve is dc . As mentioned in Chapter XII, Fig. 12-38(b), the partial pressure of water for the solution d is the same as that in the binary system B - B_1 - H_2O at the same temperature. In the H_2O -A system the saturating solid phase is the higher hydrate A_2 , with the solubility a . The solubility curve in presence of B is ab , and at b the lower hydrate becomes stable in equilibrium with solution. But before the vapor pressure can be lowered sufficiently for anhydrous A to replace A_1 , the solution becomes saturated with B, at the point c . The points b , c , and d are isothermally invariant solutions, each saturated with two solids.

If the solution P is evaporated at constant T , it begins to precipitate B_1 on the curve ed . When the liquid reaches point d , it becomes invariant in composition while B_1 is dehydrated to B. During this process the total composition (condensed phases) moves from x to y , but the liquid, point d , remains constant both in composition and in its actual quantity. That even the quantity of the liquid remains unchanged follows from the fact that the component A, present only in the liquid phase, is not involved in the phase changes. It is therefore as though the evaporation from x to y did not con-

cern the liquid phase at all, but only the solid hydrates; this is an example, then, of an equilibrium of lower order, as discussed in Chapter I–H. Point d is therefore an “inevaporable solution” as long as any hydrate B_1 is present. When the evaporation has brought the total composition to point y and the solution is saturated only with B , the liquid proceeds along the curve dc , to point c , when it precipitates simultaneously a mixture of A_1 and B in the proportions $A_1/B = qB/A_1q$. Similar evaporation of solutions on the left side of the line Ccq leads to precipitation successively of A_2 and A_1 and finally to the point c , which is therefore the drying-up point of the isotherm. Compositions in the isothermally invariant triangles I, II, III, and IV consist, at equilibrium, of three phases, $A_2 + b + A_1$, $A_1 + c + B$, $B_1 + d + B$ and $A + A_1 + B$, respectively.

Fig. 13–16(b) is a variation of 13–16(a) such that the drying-up point of the isotherm is a solution c precipitating two hydrates, A_1 and B_1 ; the vapor pressure of solution c , in other words, is higher than the decomposition pressures of these hydrates in their respective binary systems of salt and water at the specified temperature. If the isothermal evaporation is continued after the final disappearance of the liquid phase (experimentally this means expansion of the vapor phase at constant T), the pressure drops and one of the hydrates must decompose to give either the equilibrium $A + A_1 + B_1 + \text{vapor}$ or the equilibrium $B + B_1 + A_1 + \text{vapor}$. Which of the two arrangements will be obtained, however, cannot be predicted from the “solubility isotherm” itself, for this is simply the diagram above the line A_1B_1 . The arrangement will be that shown in Fig. 13–16(b) if the decomposition pressure of A_1 (or p_A) is higher than that of B_1 (or p_B). Continued removal of the vapor now causes further dehydration of A_1 until the composition of the solid mixture (always with vapor ignored) reaches the line AB_1 , when all A_1 is dehydrated. Now the vapor pressure can drop to p_B and B_1 begins to be dehydrated, giving the mixture $B + B_1 + A + \text{vapor}$. The vapor pressure again remains fixed, now at p_B , until all of B_1 is dehydrated, and it then drops to zero.

The isotherm of Fig. 13–16(b) therefore has three isothermally invariant regions of fixed vapor pressure: III with the vapor pressure of solution c , II with p_A and I with p_B , the latter two being fixed by the separate binary systems. Each of the two faces representing salt-water binary systems, in the isothermal P/c prism of such a ternary system is, in other words, similar to Fig. 7–30, if the vapor is pure water.

Under the vapor pressure of the system, therefore, the isothermal trapezoid AA_1B_1B is divided at equilibrium by the diagonal AB_1 ; $A + B_1$ is the stable pair while the combination $B + A_1$ is unstable. If the hydrates A_1 and B_1 are assigned the formulas AC and BC the chemical relation involved

is seen to be the simple displacement $A + BC \rightleftharpoons AC + B$. The possible inversion of pair stability by change of pressure at constant temperature has already been mentioned for this type of system under Fig. 12-53.

3. Double Salts, or Compounds of A and B

These are binary if anhydrous, and ternary if hydrated. Fig. 13-17 shows an anhydrous double salt which appears at T_1 and becomes congruently soluble (in C, or H_2O) at T_3 . The temperature range from the 4-phase

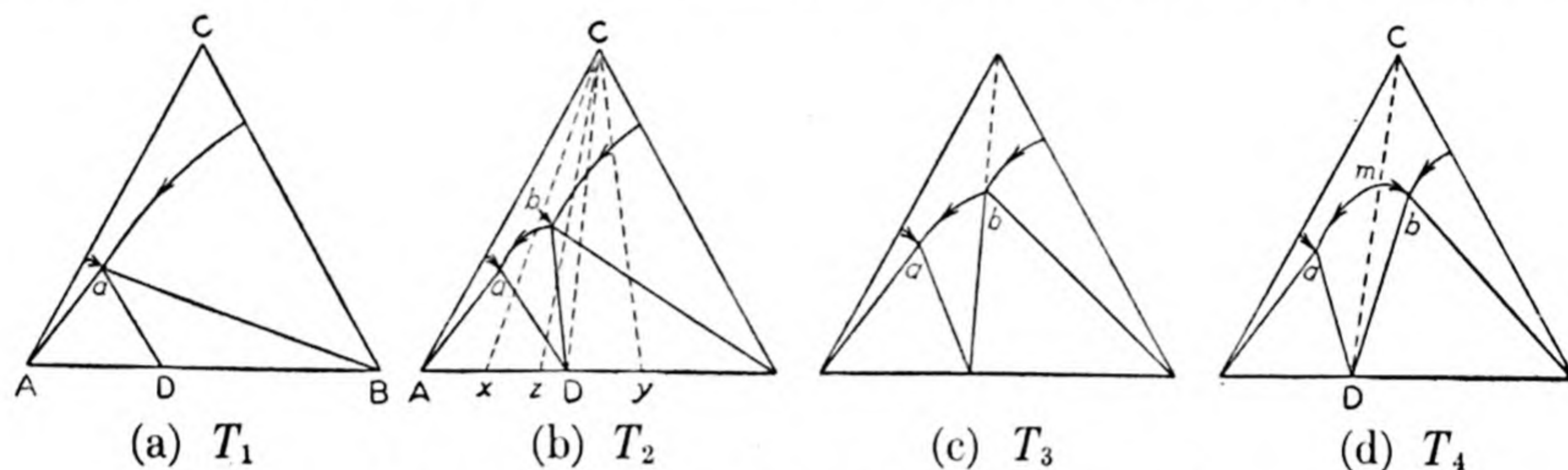


FIG. 13-17. Anhydrous binary compound.

invariant point at T_1 ($L + A + D + B$) to T_3 , where the compound becomes congruently soluble, is sometimes known as the *transition interval* of the double salt.¹⁴ T_1 may be considered to be one of the condensed invariants P of Figs. 12-42, 43, 45, 69. According to the principle explained in connection with Fig. 13-11, a mixture of solid D and water at T_4 gives either an unsaturated solution (on the line mC) or the point m , a solution saturated with D, and excess of D. Point m is the solubility of D in water, at T_4 . But below T_3 , a solution saturated with D cannot be prepared from water and D. The addition of a small amount of water to D, at T_2 , decomposes some of the double salt and forms the solution b saturated with both D and B. If addition of water is continued, all of D is decomposed to give a solution saturated with B alone. At this temperature D does not have a (stable) solubility in pure water; saturated solutions of D are possible only on the curve ab , containing an excess of the component A compared to the ratio of A to B in D.

The section CmD at T_4 is quasi-binary, and such a section appears only when the double salt is outside its transition interval. If the solution m , at T_4 , is evaporated at constant T , it dries up to D as sole solid phase. If any solution on the curve ab , at T_2 , is evaporated, it produces D as pure solid phase only until the total composition, moving along the line Cx , enters the triangle AaD , when A begins to be precipitated with D. An incongruently soluble compound can therefore be obtained pure by crystalliza-

¹⁴ W. Meyerhoffer, *Z. phys. Chem.*, 5, 97 (1890).

tion from solution only over a restricted range of evaporation, and with limited yield. Moreover, the congruently soluble compound (at T_4) can be washed with the solvent without decomposition, whereas the incongruently soluble compound (at T_2), even if correctly prepared, cannot be washed with the solvent without decomposition, for, as already pointed out, the total composition would then enter the 3-phase triangle DbB .

Solution m , on the line CD , is said to be congruently saturated with D and dries up to D in isothermal evaporation. Similarly, solution a in Fig. 13-17 is congruently saturated with its two solids because the line Ca cuts the line joining the solids, AD ; on isothermal evaporation it dries up to leave a mixture of the solids with which it is saturated, in the proportions given by point a itself. Solution b on the other hand, at $T < T_3$, is therefore seen to be incongruently saturated with its two solids; on isothermal evaporation, with equilibrium maintained, it dries up not to a mixture of D and B , its saturating solids, but to A and D .

Above T_3 , therefore, the isotherm has two congruent drying-up points in isothermal evaporation, a and b . Liquids reaching the curve ab , in Fig. 13-17(d), precipitate D on further evaporation, and, losing water and D simultaneously, they move away from point m , the point of maximum W_l on the curve, on either side. Hence all liquids on the left of the line CD dry up, congruently, at point a , to leave the mixture $A + D$; and those on the right dry up at point b to a mixture of D and B . The points a and b are both minima of W_l for the isotherm. Below T_3 , however, point b is an incongruent drying-up point for compositions in the triangle CDB , and point a the congruent drying-up point for the triangle ACD . If an unsaturated liquid on the line Cy is evaporated, it precipitates B while its composition follows the curve to b . At this point the composition of the solution (W_l , for example) remains constant, while the reaction $L + B \rightarrow D + \text{water vapor}$ proceeds until all the liquid is consumed, to leave the mixture y , of $D + B$. If a liquid on the line Cz is evaporated, it similarly reaches point b , where it is isothermally invariant until solid B is consumed. Then the liquid, saturated with D alone, travels on ba toward a , precipitating D , and at a it dries up, congruently and invariantly, to the mixture z , of $A + D$. If complete equilibrium is not maintained, and the solid B is not given sufficient time to redissolve at point b , then whatever the original composition of the liquid reaching point b , the final drying-up point is a , leaving a non-equilibrium mixture of three solids, $A + D + B$. The same remark applies to Fig. 13-16 (a), with regard to solutions halting at points b and d on their way to point c .

Since these isotherms are "condensed diagrams," the vapor phase is always present, and the solutions a and b of Fig. 13-17 are actually parts of

isothermally invariant 4-phase equilibria. When they are subjected to isothermal evaporation or dilution, the effective variable is therefore the pressure (vapor pressure), and the experimental stress is strictly the change of volume of the vapor phase, which consists of pure water. The 4-phase equilibria of Chapter X, Figs. 10-23 and 10-24, have been illustrated in Chapters XI and XII by a number of isobaric invariants, with T as the variable. In the isothermal evaporation of aqueous salt systems the drying-up points are illustrations of isothermal invariants, both type Q_A and type Q_B , with the vapor pressure as the variable. Point a of Fig. 13-17, a congruent drying-up point, is an example of type Q_A , a triangular invariant terminal here in respect to liquid a , the interior phase of the triangle ACD . The isothermally invariant reaction is $L(a) \rightleftharpoons A + D + C$ (water vapor) + volume. Continued expansion must lead to disappearance of the liquid, whereupon the vapor pressure will fall. Point b in Fig. 13-17(b), an incongruent drying-up point, is an example of type Q_B , a quadrangular invariant with the diagonal reaction $L(b) + B \rightleftharpoons D + C$ (water vapor) + volume. Expansion now leads to disappearance of either L or B depending on the composition, and the vapor pressure is constant until one of these phases is consumed.

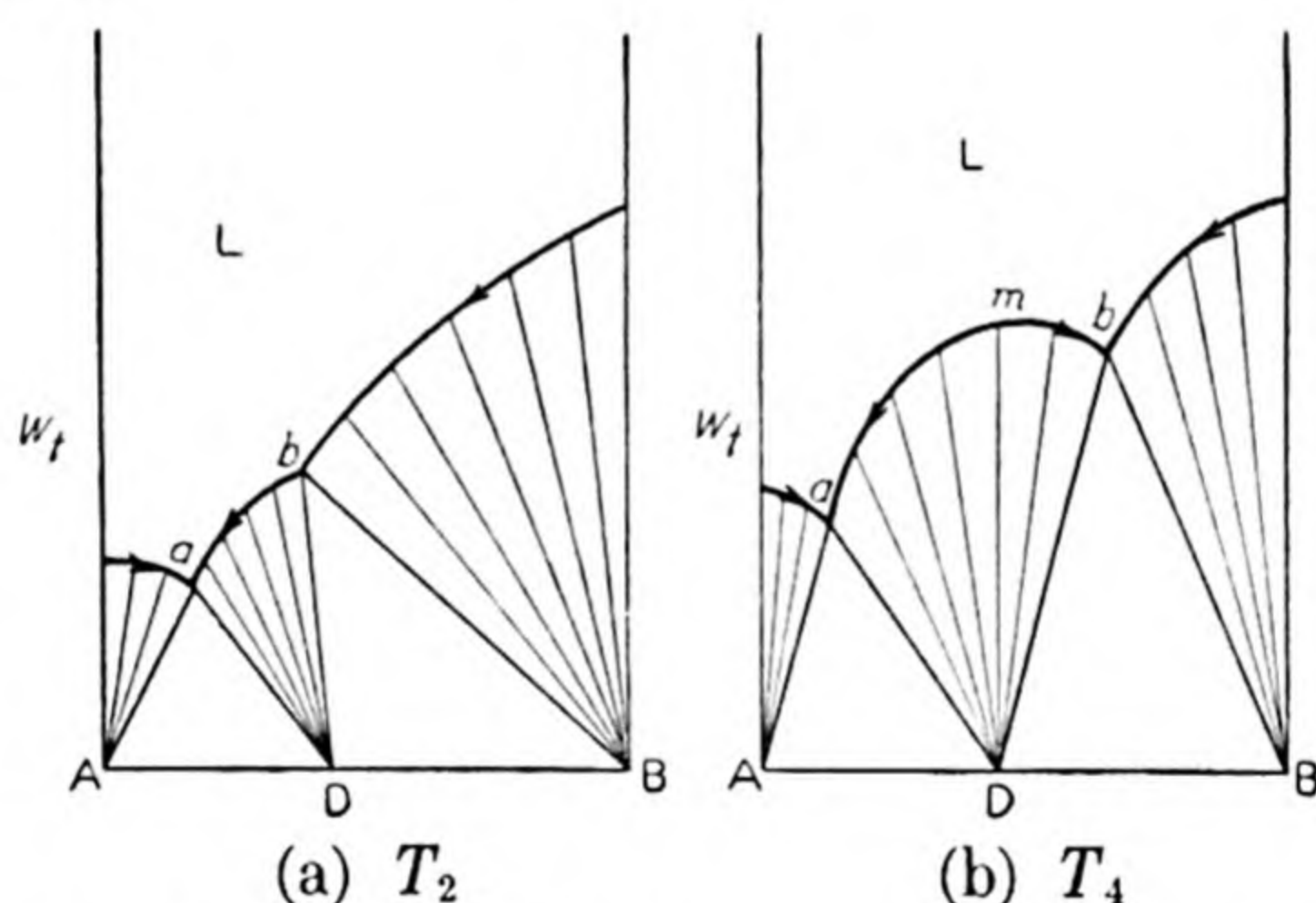


FIG. 13-18. Jänecke diagrams of Fig. 13-17.

The analogy between the variable W_t for isothermal evaporation or isothermal dilution for such a ternary system and the variable T for the isobaric freezing or melting of a binary system, is again seen if Figs. 13-17(b) and (d) are plotted, as in Fig. 13-18, on the Jänecke type of diagram. When W_t for the saturated solution of D is raised to the value b of Fig. 13-18(a), the incongruently soluble double salt decomposes into $L + B$, in the isothermally invariant reaction $D + H_2O \rightleftharpoons L + B$, just as in a binary system an incongruently melting compound decomposes at a certain T into $L +$ a component (say B), in the isobarically invariant reaction $D + \text{cals} \rightleftharpoons L + B$; the addition or removal of water in the first case cor-

responds to the addition or removal of heat in the second case. In Fig. 13-18(b) the composition of the double salt, in respect to proportions of A and B, is given by the maximum (in respect to W_l) of its solubility curve, just as in a binary melting point diagram it is given by the maximum (in respect to T) for its melting point curve.

The analog of point (d) in Fig. 13-16(a), an invariant point in isothermal evaporation not involving the component A, is a polymorphic transition of the pure component B in the $(T/c)_P$ diagram of the binary system A-B; a difference in hydration is the analog of polymorphism.

Fig. 13-19 (schematic) represents a system with double salt in two degrees of hydration. Both the hydrates are incongruently soluble at the tempera-

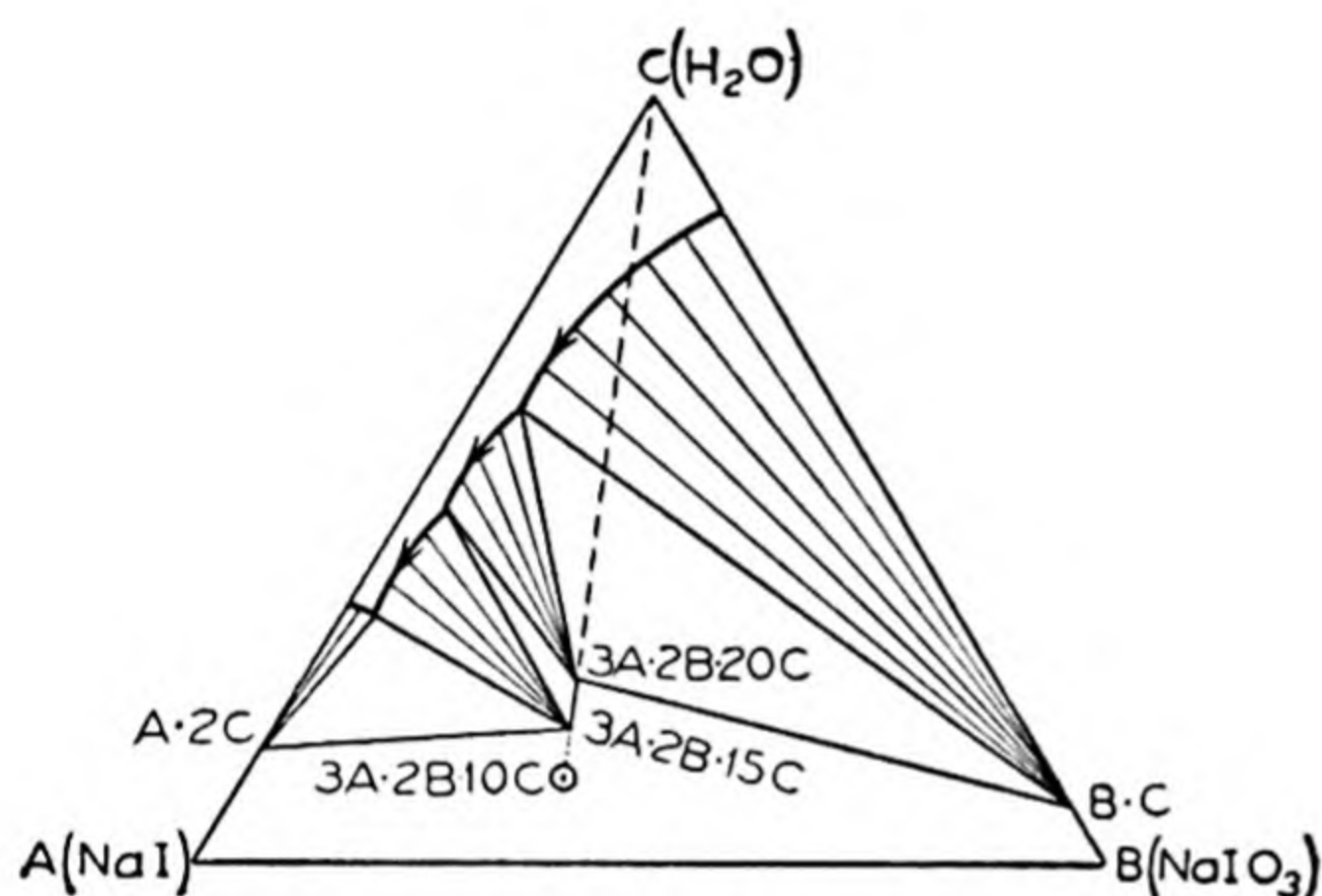


FIG. 13-19. Schematic isotherm, at 25°, of system NaI-NaIO₃-H₂O.

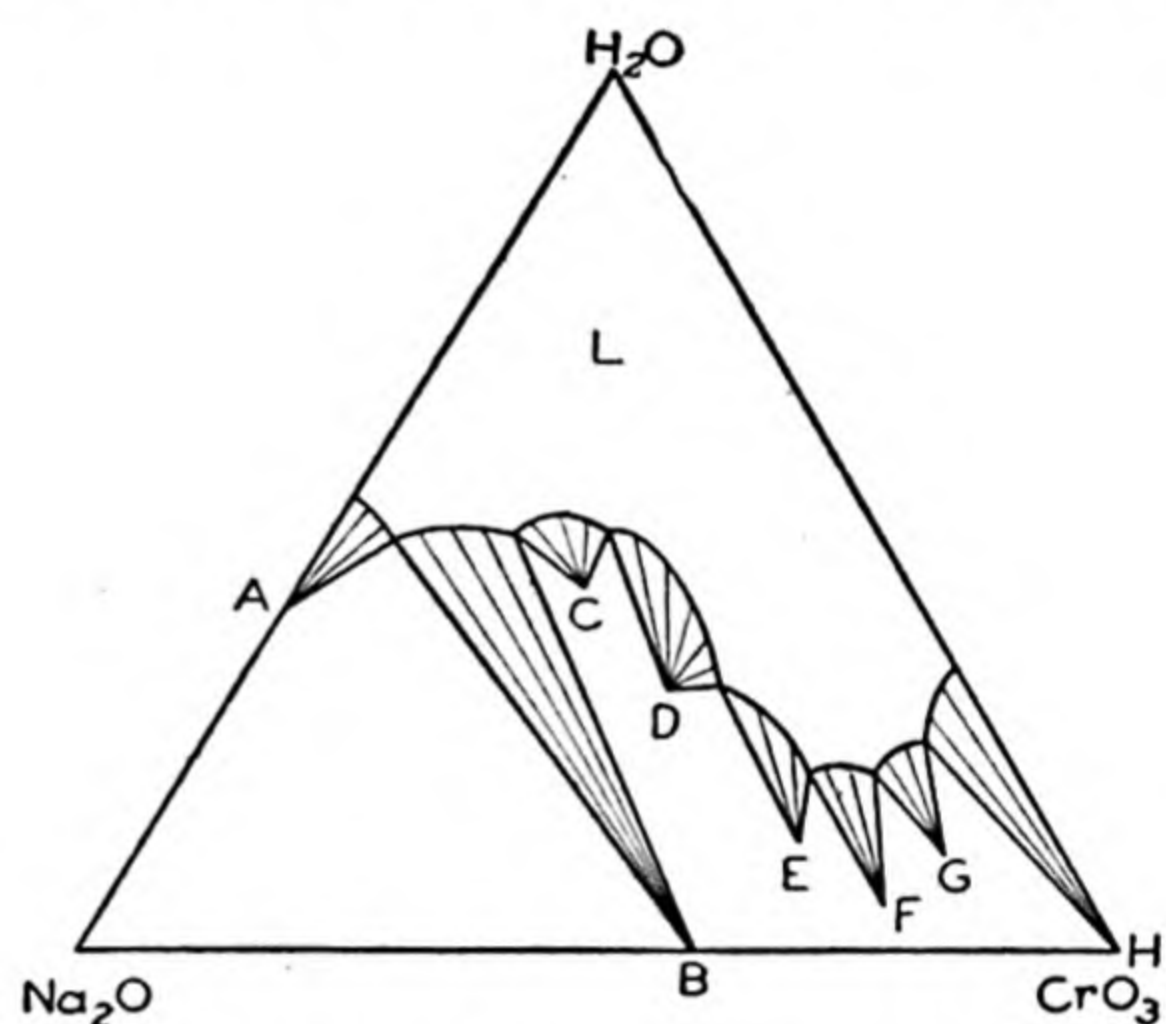


FIG. 13-20. Schematic isotherm, at 30°, of system Na₂O-CrO₃-H₂O.

ture of the isotherm, and the only congruent drying-up point is the solution saturated with NaI·2H₂O and 3NaI·2NaIO₃·15H₂O. At 40°, the higher hydrate of the double salt has disappeared, and a decahydrate has become stable in equilibrium with liquid, below the field for the compound 3NaI·2NaIO₃·15H₂O.¹⁵

Fig. 13-20 (also schematic) shows the system Na₂O-CrO₃-H₂O at 30°.¹⁶ The solid phases are A-Na₂O·3H₂O, B-Na₂O·CrO₃, C-2Na₂O·CrO₃·13H₂O, D-Na₂O·CrO₃·4H₂O, E-Na₂O·2CrO₃·2H₂O, F-Na₂O·3CrO₃·H₂O, G-Na₂O·4CrO₃·4H₂O, and H-CrO₃.

The points on these diagrams, Figs. 13-16 to 13-20, representing liquid saturated with two solids, are isothermally invariant, the properties of the liquid being independent of the amounts of the solid phases present. In certain cases these mixtures of liquid + two solids may be used to give solutions of definite acidity at constant temperature, as in the systems

¹⁵ J. E. Ricci, *J. Am. Chem. Soc.*, **56**, 295 (1934).

¹⁶ F. A. H. Schreinemakers, *Z. phys. Chem.*, **55**, 71 (1906).

$\text{HgO-CrO}_3\text{-H}_2\text{O}$ ¹⁷ and $\text{K}_2\text{O-CrO}_3\text{-H}_2\text{O}$,¹⁸ and hence also in Fig. 13-20. Such solutions are therefore completely "buffered" with respect to addition of the components of the system.

4. Solid Solution of the Components A and B (Isomorphous Salts).

If the two salts, always with common ion, are isomorphous, they may form solid solution as saturating phase. Fig. 13-21 shows the case of continuous

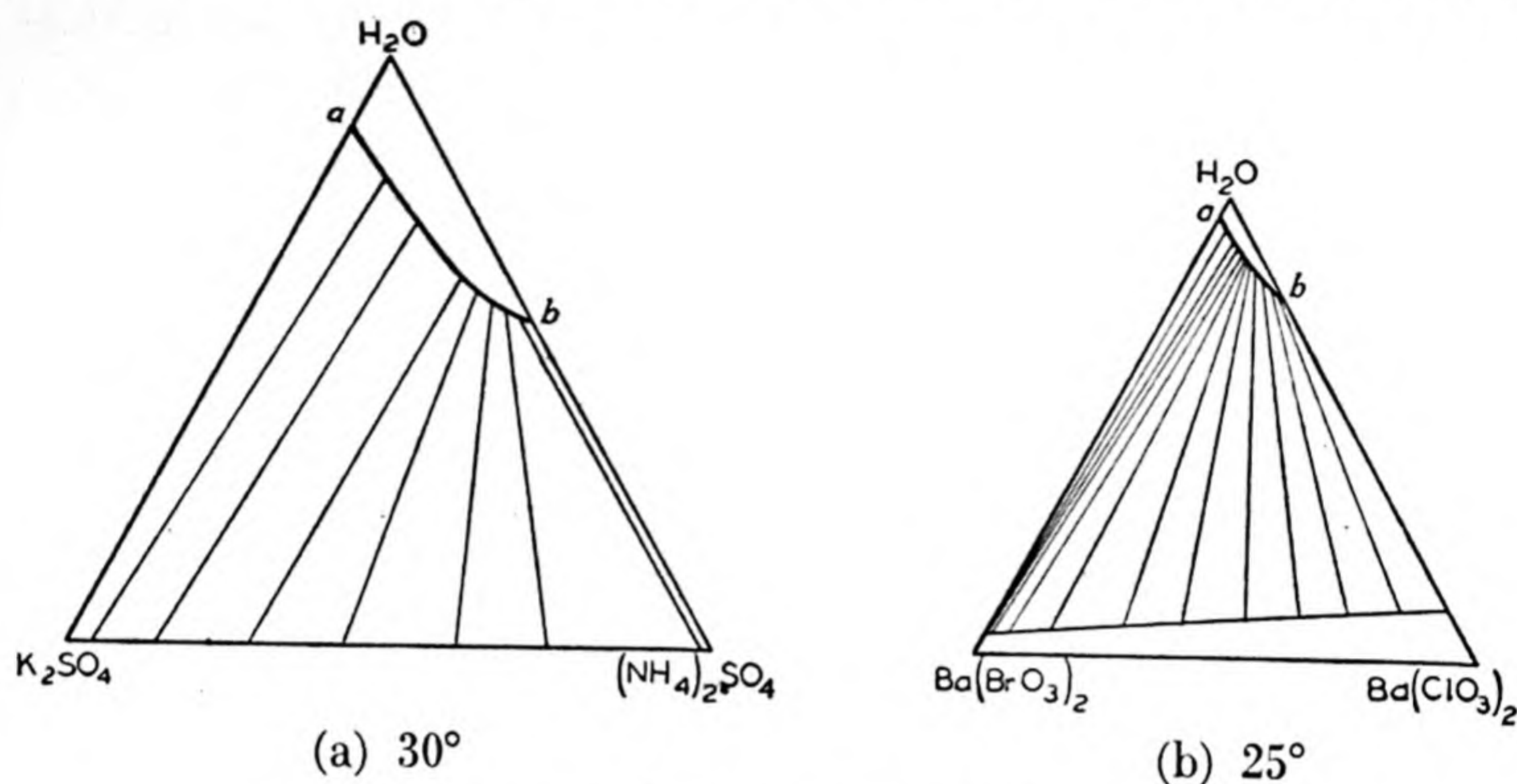


FIG. 13-21. Continuous solid solution of salts.

solid solution between anhydrous salts in (a), and between isomorphous hydrates in (b). In these cases the solubility curve is continuous from *a* to *b*, and the solid phase is a continuous solid solution lying on the line $\text{K}_2\text{SO}_4\text{-(NH}_4)_2\text{SO}_4$ in Fig. 13-21(a),¹⁹ and on the line joining the two monohydrates in 13-21(b).²⁰ Tie-lines join the two continuous curves of liquid and saturating solid.

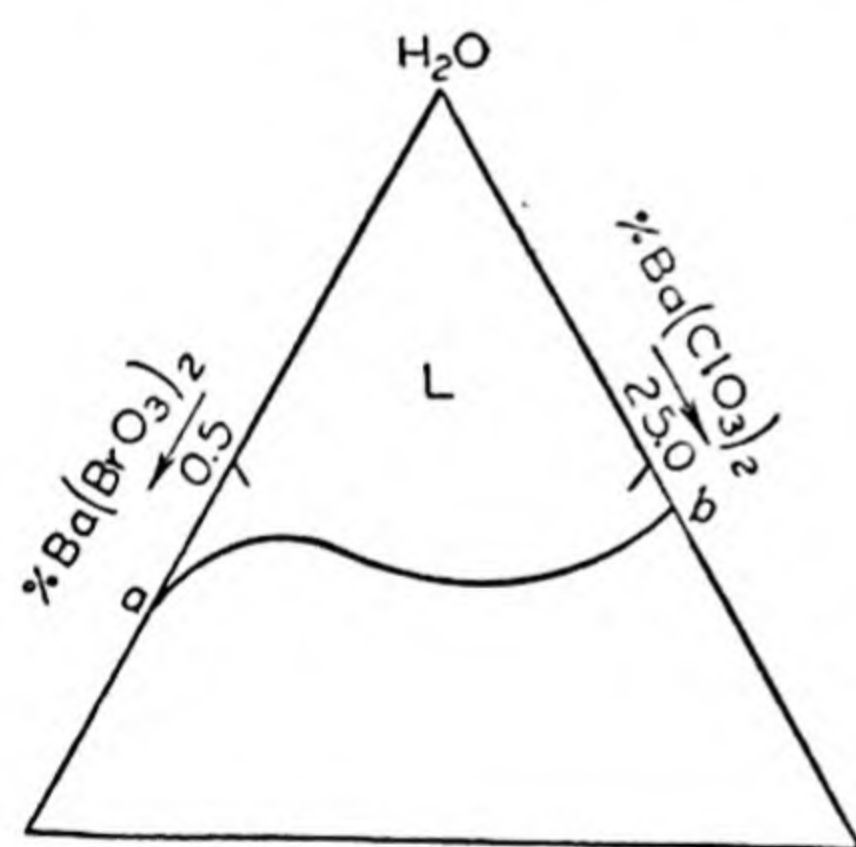


FIG. 13-22. Detail of Fig. 13-21(b).

The interest in these isotherms lies principally in the shape of the liquid curve and in the disposition of the tie-lines, for both these aspects involve the change in the activity of the components with the composition of the solid solution. The shape of the curve of the system in Fig. 13-21(b), seen in the enlargement in Fig. 13-22, is typical for the case in which the solubilities of the two salts are very unequal. The curve is S-shaped, but the minimum

¹⁷ A. J. Cox, *Z. anorg. Chem.*, **40**, 146 (1904).

¹⁸ J. Koppel and R. Blumenthal, *ibid.*, **53**, 228 (1907).

¹⁹ A. Weston, *J. Chem. Soc.*, **121**, 1223 (1922).

²⁰ J. E. Ricci and S. H. Smiley, *J. Am. Chem. Soc.*, **66**, 1011 (1944).

in water content is only apparent, caused by the unequal scales of the two axes. Experimentally the water content decreases continuously from a to b , which is also the direction of isothermal evaporation.

The behavior of the tie-lines is the problem of the distribution of the components A and B between their saturated aqueous solution and the saturating binary solid solution. Even the solid solution of two hydrates may be considered binary, the components being the individual hydrates,

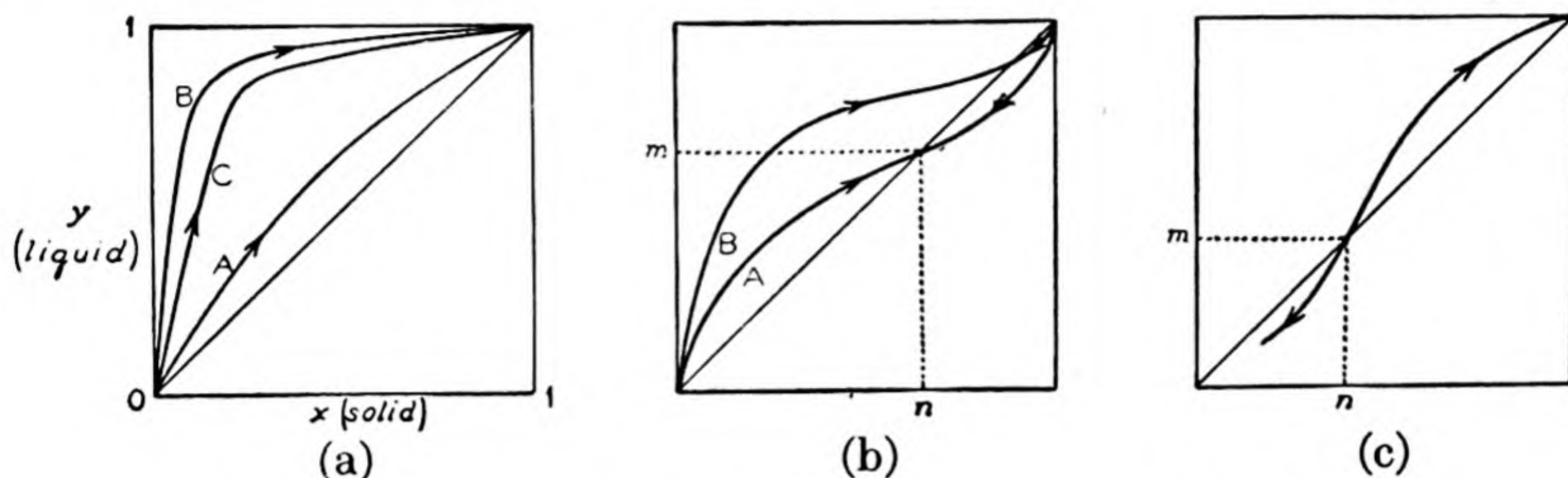


FIG. 13-23. Distribution curves, Roozeboom Types I-III.

(a) Type I

A. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} - \text{MgSO}_4 \cdot 7\text{H}_2\text{O} - \text{H}_2\text{O}$ (17-19°)²²

B. $\text{K}_2\text{CrO}_4 - \text{K}_2\text{SO}_4 - \text{H}_2\text{O}$ (25°)²³

C. $(\text{NH}_4)_2\text{SO}_4 - \text{K}_2\text{SO}_4 - \text{H}_2\text{O}$ (25°)¹⁹

(b) Type II

A. $\text{KBr} - \text{KCl} - \text{H}_2\text{O}$ (25°)²⁴

B. $\text{KFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{H}_2\text{O}$ (17-19°)²²

(c) Type III

$\text{PbCl}_2 - \text{PbBr}_2 - \text{H}_2\text{O}$ ²⁵

such as two alums. This distribution is best studied on the basis of the plot of mole fraction (y) of one of the salts (here the more soluble one) in the total of dissolved salts (water neglected) in the liquid phase, against the corresponding fraction of the same salt in the solid phase (x). If the solid solution is continuous, three types of distribution are possible, known as the Roozeboom Types I, II, and III²¹ (Fig. 13-23).

In Type I, y is always greater than x . If the solid solution is ideal, the curve is always of this type and symmetrical in respect to the diagonal of the diagram; the curve may then be calculated theoretically from the solubilities of the individual salts, with certain plausible assumptions concerning

²¹ B. Roozeboom, *Z. phys. Chem.*, **30**, 385 (1899), for binary systems; *ibid.*, **8**, 521 (1891), for the present ternary case.

²² R. Hollmann, *Z. phys. Chem.*, **37**, 193 (1901).

²³ M. Amadori and G. Pampini, *Att. Accad. Lincei*, [5], **21** [I], 667 (1911).

²⁴ M. Amadori and G. Pampini, *ibid.*, **20**[I], 475 (1911).

²⁵ G. Meyer, *Rec. trav. chim. Pays-Bas*, **42**, 301 (1923).

the activity coefficients of the ions in the aqueous solution.²⁶ As the solid solution deviates from ideality, as in system C of Fig. 13-23(a), a dissymmetry is introduced. If the deviation is in the direction of repulsion between the components in the solid solution, Type II is the result, in which y is greater than x at the beginning of the curve and smaller than x at the end. Experimentally it is almost impossible, without mathematical analysis, to determine whether a system such as C of Fig. 13-23(a) is not actually of Type II near the upper limit. If the deviation is in the opposite direction, with attraction between the components in the solid state, we have

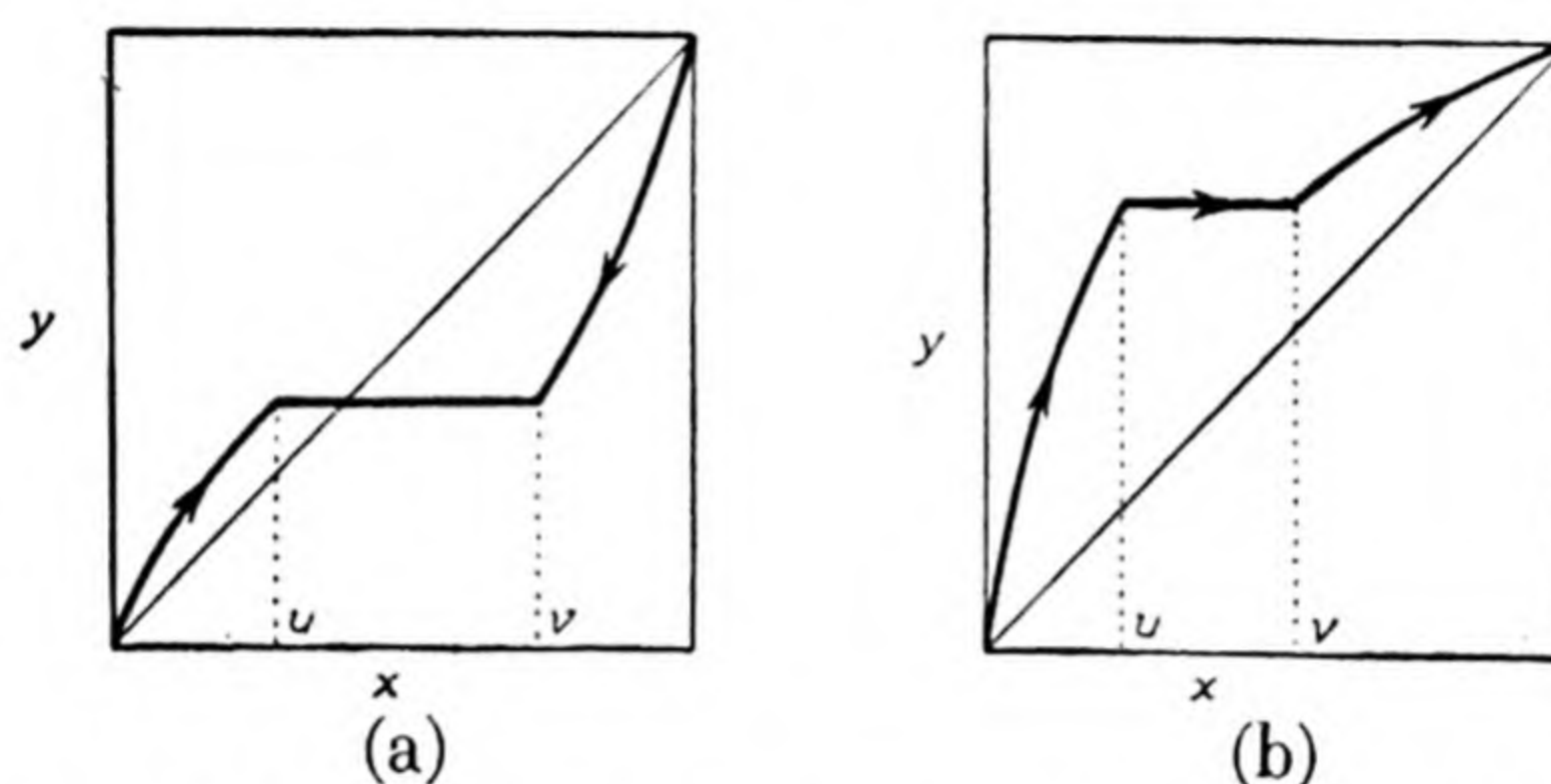


FIG. 13-24. Distribution curves, Types IV and V.

(a) Type IV

$\text{NH}_4\text{Cl}-\text{KCl}-\text{H}_2\text{O}(25^\circ)$

(b) Type V

$\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}-\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}-\text{H}_2\text{O}(17^\circ)$

Type III, with $y < x$ at the start and $> x$ at the end. The tie-lines of the triangular diagram (Fig. 13-21) show relative divergence at the solid solution for Type II and a relative convergence in Type III. Some divergence or convergence is also possible in Type I if the system is not ideal.

If the repulsive tendency (Type II) increases sufficiently, a point may be reached where a miscibility gap appears in the solid solution. This would be seen as a break in the solubility curve of the usual isothermal diagram, the break being an isothermally invariant solution saturated with two conjugate solid solutions (see Figs. 12-13 to 12-15). In the Roozeboom plot this means that the flat portion of the curve of Type II will have become horizontal, the solution being constant while the solid, now a mixture of conjugate phases, is variable (Fig. 13-24). The gap, shown extending from u to v , in Fig. 13-24(a) (system $\text{NH}_4\text{Cl}-\text{KCl}-\text{H}_2\text{O}$)²⁷ contracts as the temperature is increased and is very small at 100° , as an upper critical solution point of the solid components is being approached; in the ternary system this point would be of the type of KK' of Fig. 12-13.

²⁶ A. E. Hill, G. S. Durham, and J. E. Ricci, *J. Am. Chem. Soc.*, **62**, 2723 (1940).

²⁷ *I. C. T.*, IV-297, 385.

When the points u and v of Fig. 13-24 are one on each side of the diagonal, the system is said to belong to Type IV. If they are both on one side, as in $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} - \text{CuCl}_2 \cdot 2\text{KCl} - \text{H}_2\text{O}$ at 17° ,²⁸ it is called Type V. In either case it is possible for one of the solids to be pure, when either u or v falls on one of the sides of the diagram.

[If the binary system A-B involves one solid solution and one pure component as solid phases, or if an intermediate variable solid phase occurs, with the pure components still present as solid phases, then these five types do not suffice as a classification.²⁹]

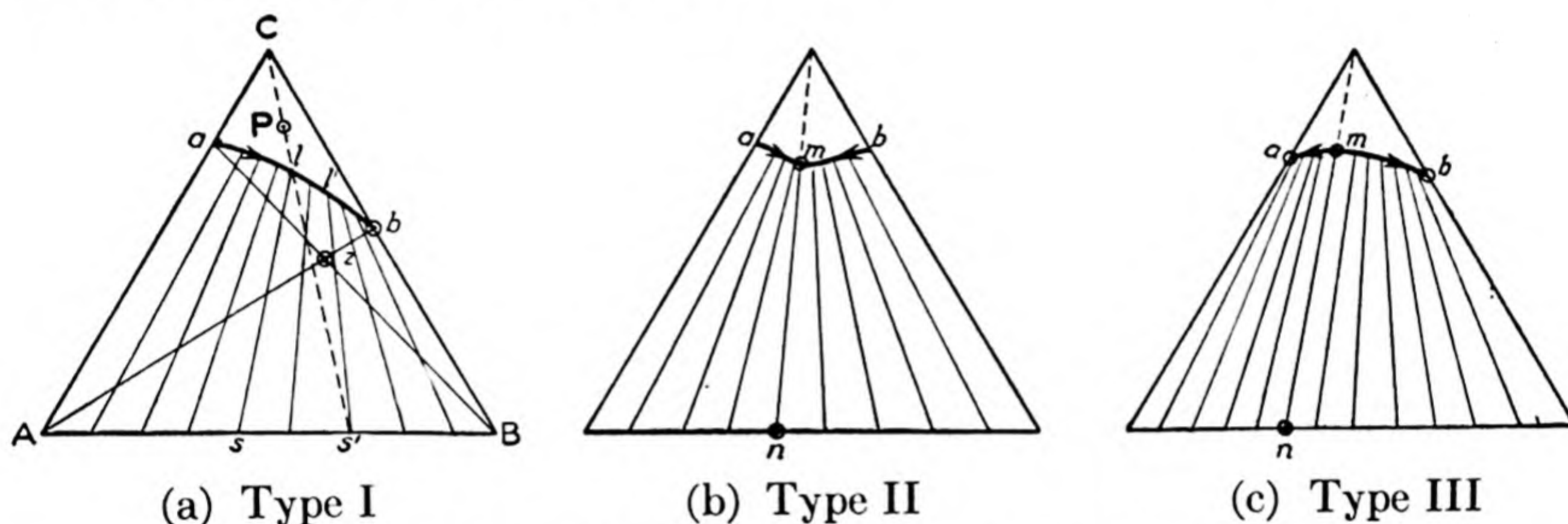


FIG. 13-25. Isothermal evaporation for Types I-III.

If the system is of Type I all the tie-lines of the triangular diagram pass, when extended, on one side of the H_2O apex. In isothermal evaporation of an unsaturated solution in such a system, then, with all the tie-lines, as in Fig. 13-25(a), passing, in extension, to the right of $C (= \text{H}_2\text{O})$, the solution must move continuously from a toward b , since the ratio of the more soluble to the less soluble component (B/A) is always greater in the solution than in the solid phase. If the solid is given time to maintain equilibrium with the solution at every point, the first solid precipitating from solution P on isothermal evaporation has the composition s ; as the liquid then moves toward b , the solid changes in composition toward B , and the last trace of liquid to dry up is l' , when the solid reaches s' . The attainment of equilibrium for a mixture such as z is generally very slow, whether it is produced by evaporation as just described or prepared from the three separate components — liquid water, and solids A and B . One way of studying the tie-line distribution in such a system is to approach the same tie-line or the same solid solution from two directions in respect to composition change. If, for example, solid A is added to solution b and solid B to solution a , to give two complexes of the same total composition z , and these are shaken at constant T , we may conclude that equilibrium has been attained when

²⁸ A. Fock, *Z. phys. Chem.*, **12**, 658 (1893).

²⁹ For examples and discussion, see J. E. Ricci, *J. Am. Chem. Soc.*, **57**, 805 (1935).

the liquid phase (and therefore, without analysis, the solid phase also) has the same composition for both samples.³⁰ Continuous grinding of the solid phase, in addition to the shaking of the mixture, is usually also necessary.

In Types II and III, shown in Figs. 13-25(b, c), the extension of one of the tie-lines passes through the H_2O corner. The solution with this tie-line, corresponding to the intersection of the Roozeboom curve with the diagonal, is congruently saturated with its solid phase, and is a point (m) of either minimum or maximum value of W_l ("water content"). On isothermal evaporation it dries up invariantly to the solid n . The *colinearity* of the three phases solid, liquid, and vapor occurs as expected, at a maximum or minimum of W_l , considered as the analog of temperature. In Type II the tie-lines on the A side of m pass to the right of H_2O , and those on the B side to the left of H_2O , so that they tend to converge toward m , the point of minimum W_l , and the direction of isothermal evaporation is toward m from either side. With complete equilibrium between solid and liquid, however, this point is not reached unless the original composition lies on the line H_2O - m . But with "effective removal" of solid (with no internal readjustment of the solid as it precipitates) point m is the effective drying-up point of the system. The opposite is the case in Type III, where the direction of isothermal evaporation is away from m , the point of maximum W_l .

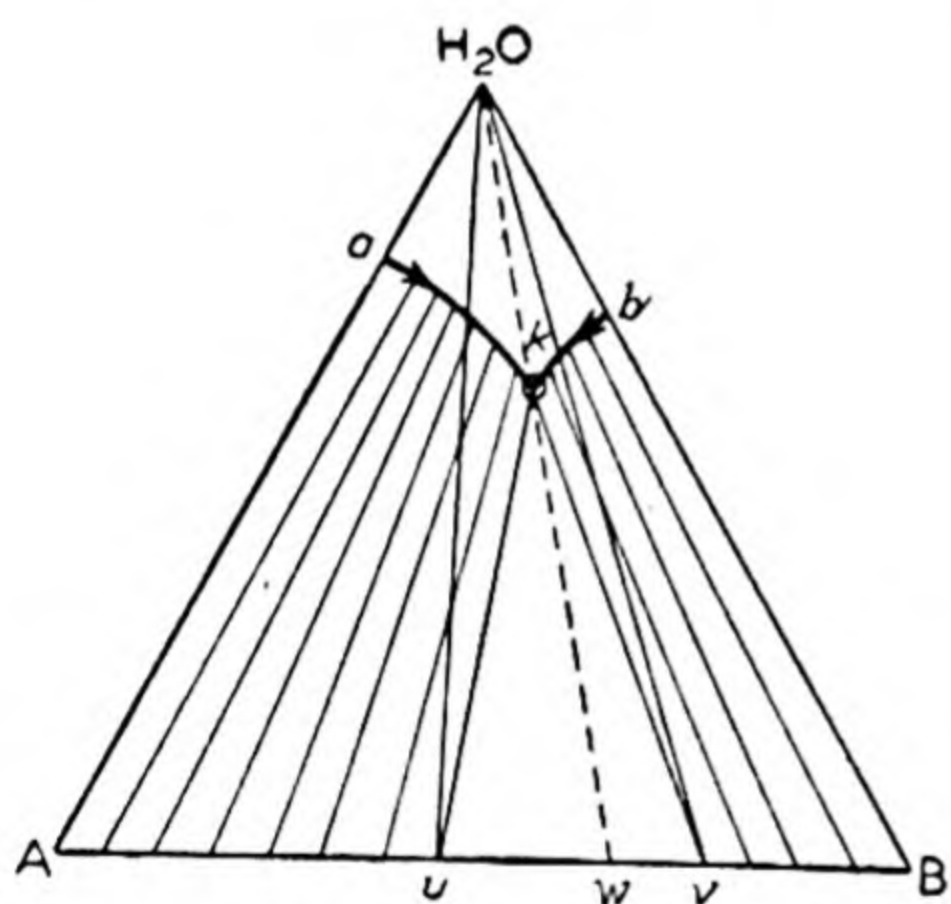


FIG. 13-26. Isothermal evaporation for Type IV.

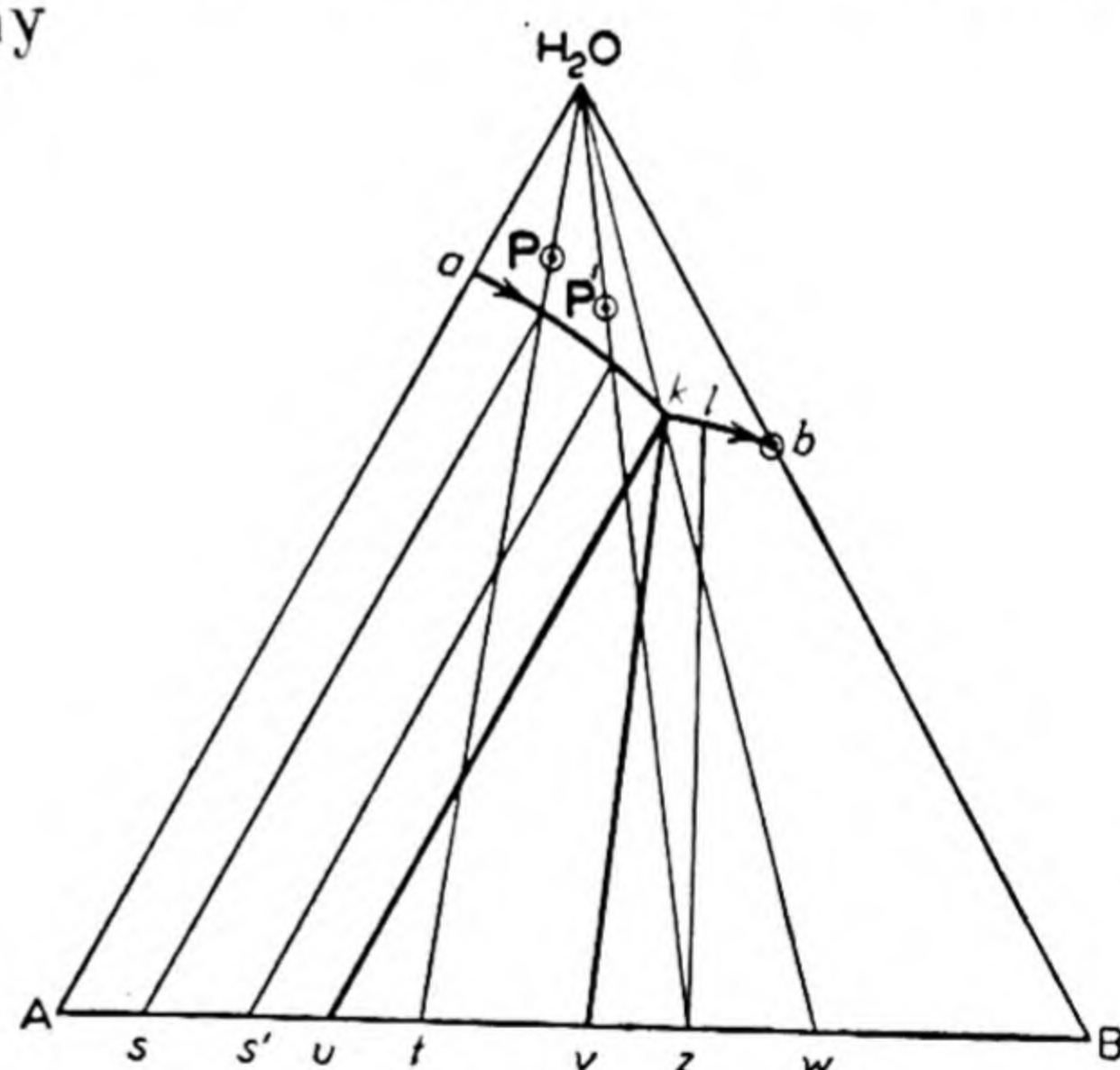


FIG. 13-27. Isothermal evaporation for Type V.

In Type IV (Fig. 13-26) the isothermally invariant point k is a solution of minimum water content. The line through H_2O and k (H_2O - w) passes through the miscibility gap (uv), and k is a congruent drying-up point for all liquids between the lines u - H_2O and v - H_2O . This is the analog of a binary system with a eutectic and limited solid solubility. In Type V (Fig. 13-27), the peritectic analog, the line H_2O - k - w does

³⁰ A. E. Hill and N. Kaplan, *J. Am. Chem. Soc.*, **60**, 550 (1938).

not pass through the MG (uv), k is not a minimum in W_l , and the direction of isothermal evaporation is from a to k and from k to b . Nevertheless the point k is the incongruent drying-up point for liquids between u - H_2O and v - H_2O . The solid formed from liquid P on evaporation starts with the composition s , and reaches the point u when the liquid reaches k ; the solution is then invariant (W_l is constant), while a second solid, of fixed composition v , is formed, and when the liquid is all consumed, a mixture of solids u and v (with total composition t) is left. The solid from liquid P' starts as s' and also reaches u when the liquid reaches k . But now solid u , not liquid, is consumed in the invariant reaction, $L + u \rightleftharpoons v + H_2O$,^{30a} and when liquid k and solid v are the only phases left, the liquid moves on and disappears at the point l when the solid reaches point z . For liquids between v - H_2O and w - H_2O , then, point k is an isothermally invariant point in their isothermal evaporation, but not a drying-up point. In Fig. 13-26, k is congruently, in Fig. 13-27 incongruently, saturated with its two solid solutions, u and v .

As analogs of isobaric freezing point diagrams of binary solid solutions, with W_l as the variable in place of T , Type I corresponds to the simple "ascendant" binary system, while Types II and III correspond to "azeotropic" systems. Type IV corresponds to limited solid solubility with a eutectic, and Type V to the peritectic case. Type III, like its binary analog of a continuous solid solution of maximum melting point, is a rare case; the only familiar example seems to be that of $PbCl_2$ - $PbBr_2$ - H_2O .^{30a}

If a sample of A contains a small percentage of B , "purification" by either of the methods discussed under Fig. 13-11 leads to enrichment in A in all types but III, in which the liquid has a higher ratio of A/B than the solid, on the A side. A sample of B contaminated with a small amount of A , on the other hand, becomes purer only in the related cases II and IV.

If the interaction involved in Type III becomes very marked, the steep portion of the curve in Fig. 13-23(c) may become vertical. This would mean a variable solution in equilibrium with a solid of fixed composition, which would therefore be a compound.^{30b} (Hence such distribution diagrams may be substituted, at times with superior convenience, for the ordinary triangular representation, since they succeed in magnifying effects on the solubility curve, as in the case of the $PbCl_2$ - $PbBr_2$ - H_2O system shown in Fig. 13-23(c), which would otherwise be difficult to see.) In such a case (Fig. 13-28, schematic, hypothetical) the curving section in Fig. 13-28(b),

^{30a} See also the study of the aqueous equilibria of permutites by F. W. Hisschemöller, *Rec. trav. chim. Pays-Bas*, **40**, 394 (1921).

^{30b} See, for example, the structural study of the solid solution $PbCl_2$ - $PbBr_2$, by G. Calingaert, F. W. Lamb, and F. Meyer, *J. Am. Chem. Soc.*, **71**, 3709 (1949).

from 0 to d indicates a solid solution, y reaching the value b in the liquid, x the value c in the solid, as seen in Fig. 13-28(a); c is the limit of solid solution in B at this temperature. The horizontal section de is the isothermally invariant solution b of Fig. 13-28(a); it is invariant, for solid mixtures between c and D. The vertical section ef is the curve ab of the triangle, the solution varying while the solid is constant, at D. The horizontal section fg is point a , for solid mixtures ranging from D to A_1 , and the vertical gh is the last curve, for saturation with A_1 alone.

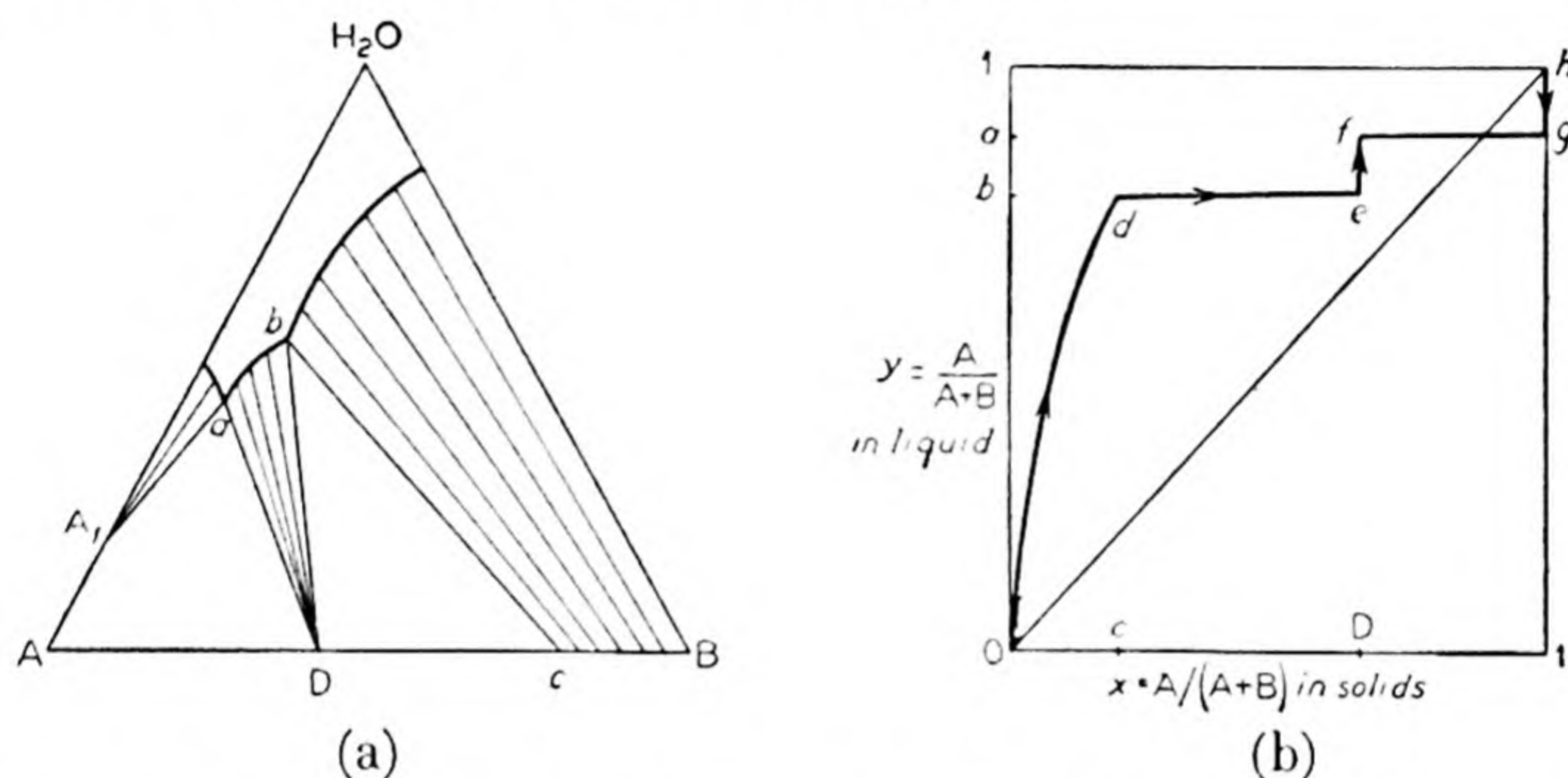


FIG. 13-28. Relation between triangular isotherm and distribution curve.

Since the water content is not shown in the Roozeboom diagram, the direction of isothermal evaporation is not immediately apparent. In Type I, Fig. 13-23(a), the direction is toward $y = 1$, since y is the percentage of the more soluble salt. Otherwise the change is always toward congruent drying-up points and in the direction of increasing concentration, and hence, as shown by the direction arrows on the curves of Figs. 13-23, 13-24, 13-28(b), toward the horizontal type of crossing of the diagonal and away from the vertical type of crossing.

Fig. 13-29 is the system $\text{Ag}_2\text{SO}_4\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ at 30° ; ³¹ cf. Fig. 12-61(a). The curve ak represents liquid saturated with an anhydrous solid solution of $\text{Ag}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$, extending from Ag_2SO_4 to point c . But this solid solution is actually continuous up to Na_2SO_4 ; the point c does not represent a discontinuity of this solid solution. The section from A to c is in equilibrium with liquid, as shown by the tie-lines to the curve ak ; and the section c to B exists as a mechanical mixture with D, or $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. As the temperature is increased to the transition point of this hydrate (32.4°), the point c moves toward B, and reaches it as the solubility curve of D, or kb , vanishes, leaving a diagram, above 32.4° , of the type of Fig. 13-21.

A binary compound (double salt) may also form solid solution with an

³¹ E. L. Simons and J. E. Ricci, *J. Am. Chem. Soc.*, **68**, 2194 (1946).

adjacent solid phase. This is the case with glaserite ($\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$) which dissolves Na_2SO_4 to a slight extent. In the system $\text{AgBrO}_3\text{--NaBrO}_3\text{--H}_2\text{O}$ ³² between 5° and 50° , the compound $\text{AgBrO}_3 \cdot \text{NaBrO}_3$ forms a continuous solid solution with AgBrO_3 , up to pure AgBrO_3 , while dissolving

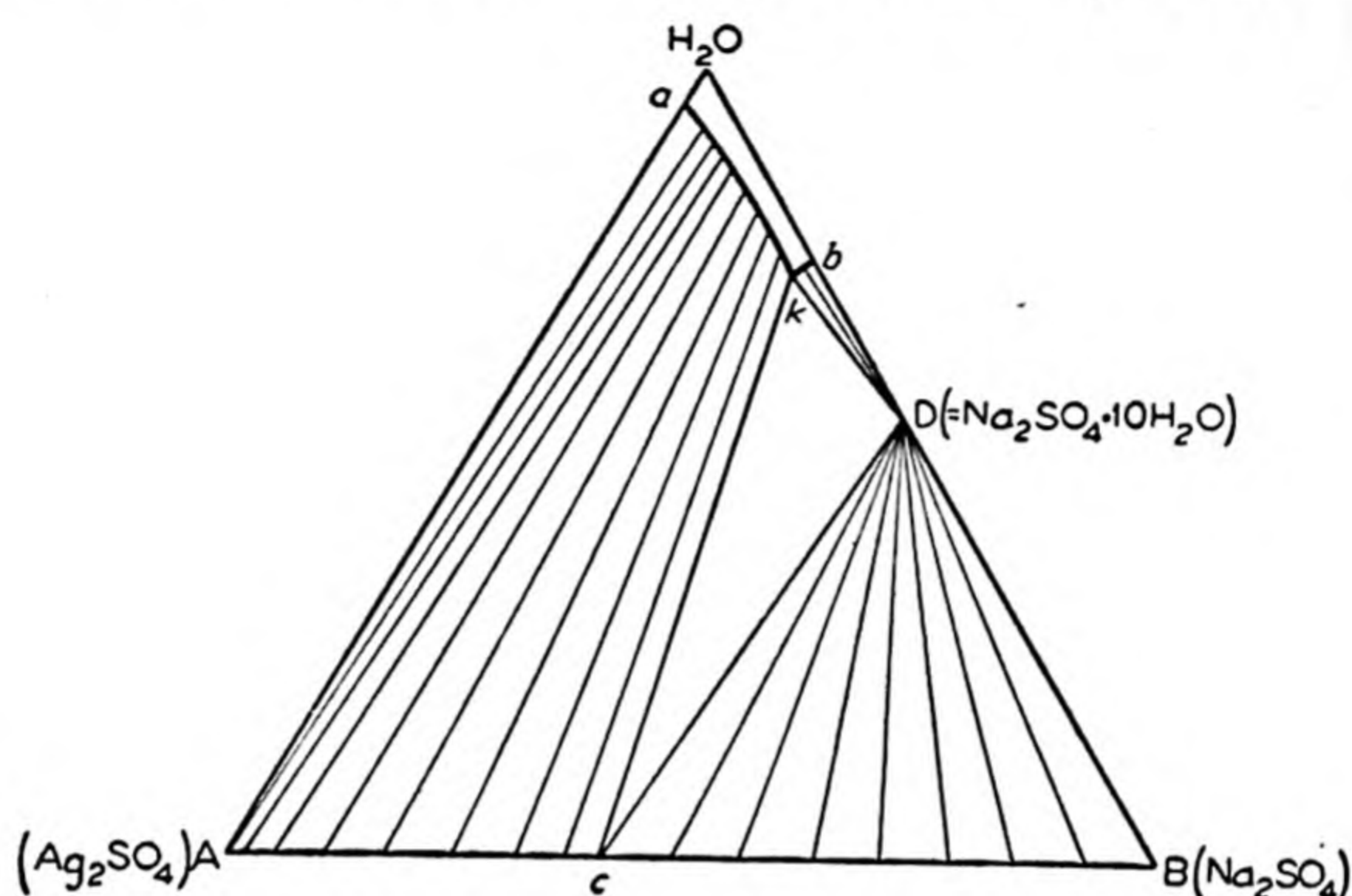


FIG. 13-29. Schematic isotherm, at 30° , of system $\text{Ag}_2\text{SO}_4\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$.

no noticeable amount of NaBrO_3 ; the NaBrO_3 phase, on the other hand, dissolves 2–3% of AgBrO_3 (Fig. 13-30, schematic). The situation here is somewhat similar to the miscibility gap of the solid solution of palladium and hydrogen (Chapter VII, Fig. 7-33). The NaBrO_3 limit of the gap is variable in composition over the temperature range studied, while the

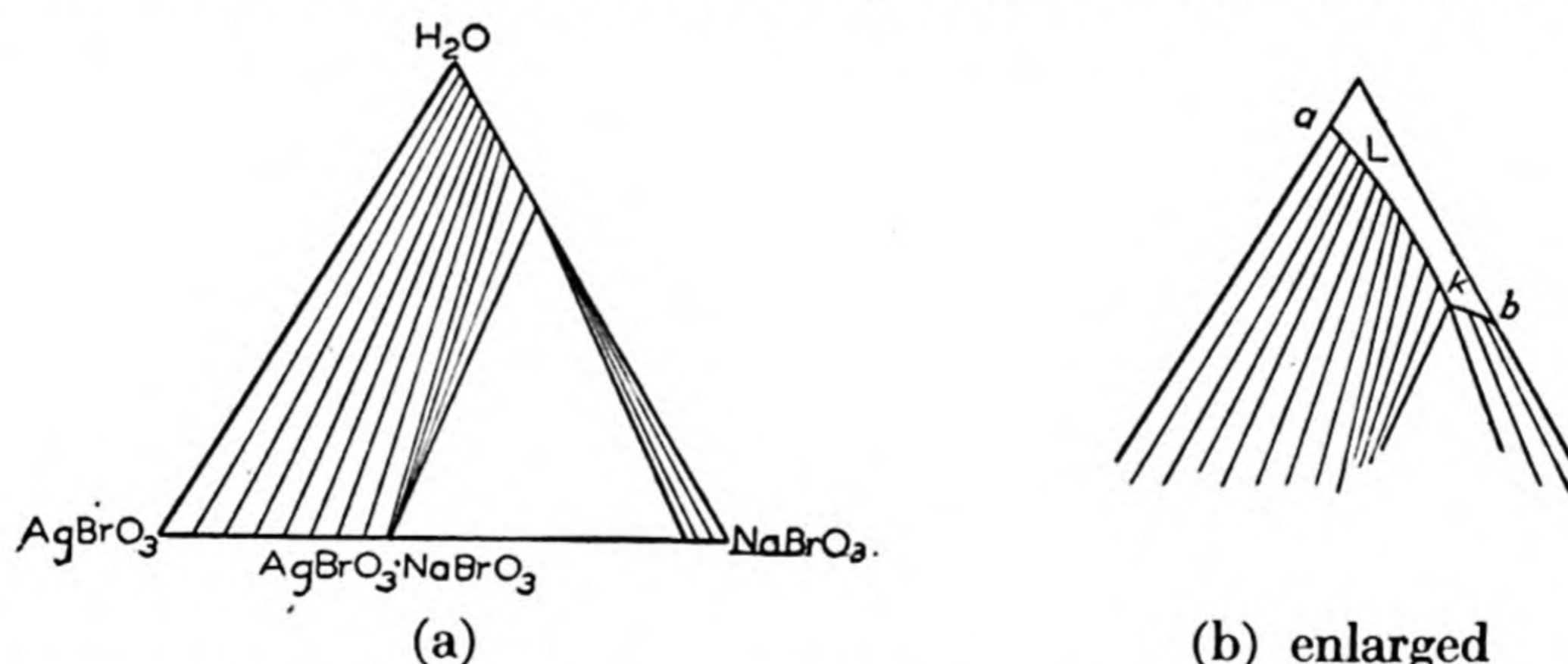


FIG. 13-30. Schematic isotherm, at 25° , of system $\text{AgBrO}_3\text{--NaBrO}_3\text{--H}_2\text{O}$.

AgBrO_3 side has the definite composition $\text{AgBrO}_3 \cdot \text{NaBrO}_3$, further emphasized by the sharp convergence of some of the tie-lines in this solid solution at this particular composition. From the disposition of the tie-lines approaching pure AgBrO_3 , it may be seen that AgBrO_3 is not expected to be purified from NaBrO_3 by recrystallization in this temperature range.

³² J. E. Ricci and J. J. Aleshnick, *ibid.*, 66, 980 (1944).

As long as only anhydrous solid phases are involved, the isothermal solubility diagram of an aqueous system of two salts gives the binary equilibrium relations of the two salts at the temperature of the isotherm. But if some of the solubility curves pertain to hydrates, as in Figs. 13-16, 13-19, 13-21(b), 13-28, then only a part, if any, of the relations of the anhydrous salts may be revealed. The isotherm of Fig. 13-19, for example (that is, its solubility curves and tie-lines), gives no information whatever on the binary system NaI-NaIO_3 . Fig. 13-29 (the region A-c-D- H_2O being the experimentally observed part) gives information on the binary system only between Ag_2SO_4 and c. Fig. 13-30 covers the whole binary system at the temperature studied.

5. *Use of Solubility in Purification and as Test of Purity*

As the purification of a sample of A is repeated, by any method whatever, two related procedures whereby the degree of purification may be followed are the determination of the melting point and the determination of the solubility in a reference solvent such as C. The effect of purification on the temperature and on the apparent range of the melting point of A was discussed in Chapters V and IX, as a problem in binary systems. If A does not form solid solution with its impurity, the apparent melting point rises with its degree of purity and finally becomes constant, that is, independent of the fraction melted (n).

The determination of the solubility of A in a reference solvent C at a specified temperature may be considered the same as the determination of its melting point at a specified concentration of C in the liquid phase. From either point of view, the solubility (or the quantity W_l , the solvent content of the saturated liquid) will depend on the purity of A and on the ratio r , of solvent to sample taken for the determination, or on the fraction n , of sample dissolved. Whether or not the individual solubility of A in the ternary liquid is decreased by the impurity or the third component B, the water content W_l (strictly the vapor pressure of the saturated solution at constant T) is affected by B in the same way, qualitatively, as the melting point of A is affected by B at constant pressure (Fig. 13-14). The variables $(W_l)_T$ and $(T)_P$ are always lowered by B as long as the solid phase does not contain B in solid solution. They rise as A is purified, and become independent of n , the fraction dissolved or the fraction melted, only for pure A. When A does form a pure solid phase (free of B), then, or when the impurity is liquid-soluble but not solid-soluble, repeated isothermal extraction with the solvent C will lead to a constant solubility independent of the ratio of solvent to sample, and the solid residue giving this constant solubility should be pure A (or a pure solvate of A, free of B). For solids of high melt-

ing point or unstable at their melting point, as in the case of many inorganic salts and complicated organic substances, this is often a dependable means of preparing a pure sample and at the same time of establishing that it is pure.

In isothermal evaporation, then, the value of W_l for saturation, or for the first appearance of a precipitate, corresponds to the temperature of initial solidification in the isobaric binary system. In reverse, the temperature for the final disappearance of solid on melting (still the same temperature, if both determinations represent the same equilibrium state) corresponds to the value of W_l for the complete solution of the sample in isothermal dilution. From the plot of the melting point as function of the fraction melted, it is possible to estimate the purity of the sample and the melting point of pure A, as mentioned in Chapter IX. Similarly, therefore, it is possible to estimate the purity of the sample and the solubility of A from the plot of W_l , the water content of its isothermally saturated solution, as function of the fraction dissolved. In both cases the calculation involves essentially the same assumptions and is correct only if these assumptions are applicable: the solid phase must be pure A and the solution, containing always all the impurity, must be ideal.

In the determination of solubilities, the fraction dissolved, for any given sample, depends on the ratio r of solvent (W) to sample ($A + B$). If W_1 is the weight fraction of solvent in the saturated solution at the ratio r_1 , and W_2 at the ratio r_2 , if S_0 is the weight fraction solubility of pure A in pure solvent, that is, $A/(A + W)$, and if x is the weight fraction of the soluble impurity B in the solid sample, we obtain the following expressions if the ratio $A/(A + W)$ is assumed independent of the presence of B in the solution:

$$x = \frac{r_1 r_2 (W_2 - W_1)}{W_1 W_2 (r_2 - r_1)}, \quad (1)$$

$$S_0 = \frac{1 - W_l - W_l x / r}{1 - W_l x / r}. \quad (2)$$

If the assumptions are applicable, these equations permit the calculation of both x and S_0 from two measurements, namely, the water content W_l of the saturated solution at two different experimental ratios of solvent to sample.

With $W_0 = 1 - S_0$, equation (2) may be rearranged as follows:

$$W_l = W_0 / (1 + W_0 x / r). \quad (3)$$

For small x this means, approximately,

$$W_l = W_0 - W_0^2 x / r. \quad (4)$$

Moreover, if n represents the fraction of sample dissolved, we have the relation

$$\frac{1}{r} = \frac{1 - W_0}{W_0} \left(\frac{1}{n - x} \right). \quad (5)$$

Hence for small x , equation (4) becomes

$$W_l = W_0 - W_0(1 - W_0)x \left(\frac{1}{n} \right), \quad (6)$$

which is the analog of equation IX-(2). If, therefore, W_l is plotted against $1/n$, the reciprocal of the fraction dissolved, or, according to equation (4), against the reciprocal of the ratio r of solvent to sample used, the intercept gives the solubility, since $S_0 = 1 - W_0$, and the slope gives x , the fraction of soluble impurity in the sample.

The limitations are also essentially the same as in the calculation through the melting point. The addition of B may cause the solvent content to rise, if solid solution is involved, as in Fig. 13-25(c), or at least to deviate from a linear function of the ratio $1/n$, even in the limit, just as in the case of the melting point. And we may have mixtures of the same ratio of A/B as that in the isothermally invariant solution k of Fig. 13-11, in which the solubility is independent of the ratio at constant T ; this corresponds to the constant melting point of a eutectic mixture at constant pressure, independent of the fraction melted. In the solubility determination a change of temperature may be used to reveal that the sample is a mixture, and the effect may be expected to be more pronounced than that of change of pressure in the melting point determination. In both cases, moreover, this distinction fails for racemic mixtures of optical isomers. [Variations of pressure and temperature cannot be used to distinguish an inactive racemic mixture or an inactive racemic solid solution (of maximum melting point, for example, and hence of minimum solubility in an inactive solvent) from a single component. It is necessary to use either visual identification of the heterogeneous nature of the mixture, if it is a mixture, or the effect, upon the sample, of an asymmetric or optically active additional component.]

The application of some of these relations in certain fields, particularly in the preparation of pure samples of unstable, biologically important substances, has sometimes been termed "solubility analysis."³³

6. Optical Isomers

If A and B are optical isomers of a substance, and C an inactive solvent such as water, the solubility isotherm is symmetrical (Fig. 13-31). The saturated solution of an optically inactive sample of the substance, point k ,

³³ T. J. Webb, *Anal. Chem.*, **20**, 100 (1948); G. M. Bennett, *Analyst*, **73**, 191 (1948). See also W. Reeve and R. Adams, *Anal. Chem.*, **22**, 755 (1950).

itself is optically inactive, whether it is saturated with a mixture, Fig. 13-31(a), a solid solution of d and l in the proportions 1:1, Fig. 13-31(b), or the racemic compound, which is always congruently soluble, Fig. 13-31(c). The first can be distinguished from the other two cases if the inactive, saturated solution is treated with any quantity of active sample of the substance, whether this be a pure isomer or any sample other than one in

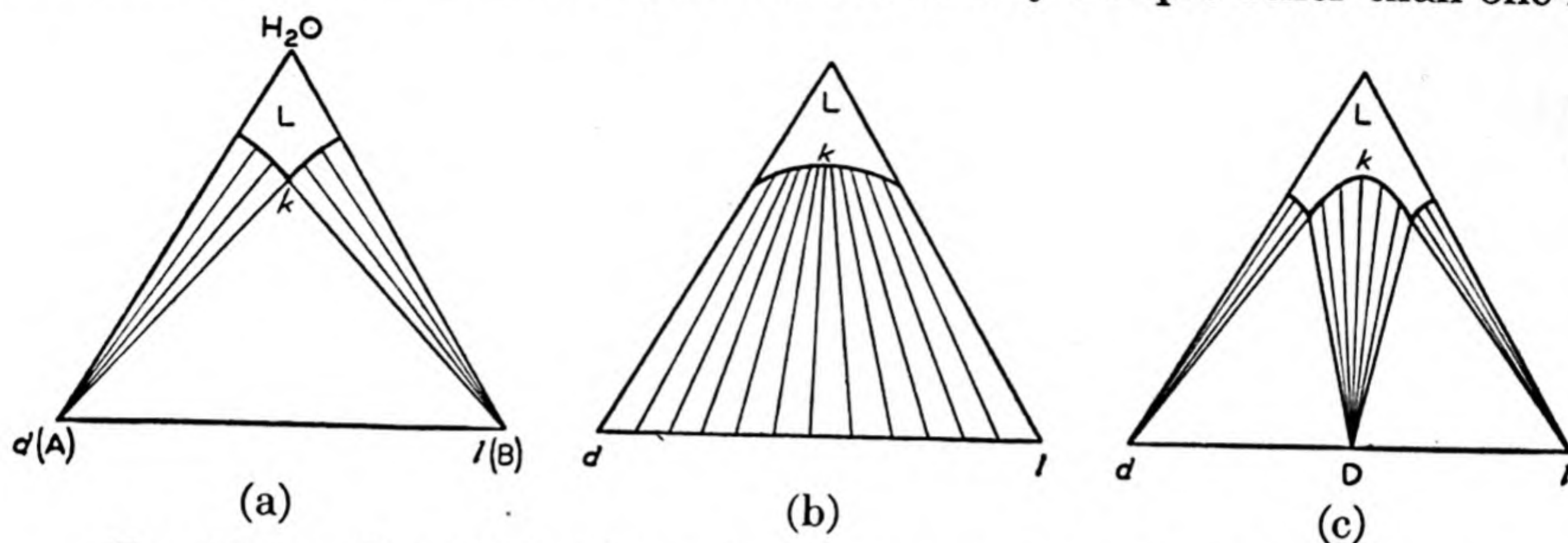


FIG. 13-31. Possible isotherms for aqueous systems of optical isomers.

which the d and l forms exactly compensate each other. Since in the first case the solution k is isothermally invariant and already saturated with both d and l , addition of excess of either form causes no change in the composition of the solution, which therefore remains inactive. In both the other cases the saturated solution develops optical activity if anything but an inactive sample is added, since the composition of the solution at its new position of equilibrium must move to one side of point k . The distinction between (b) and (c) would depend upon whether or not the continued addition of the active material leads to an "optically invariant" solution, such as that for saturation, in (c), with respect to both D and one of the active isomers. These effects, in short, are analogous to the effect of active material on the melting point of an inactive sample: no effect if the latter is a eutectic mixture, a drop if it is a solid solution of maximum melting point, and always a drop if it is a compound, rising again beyond a certain point.

If C itself is an optically active solvent, the diagrams will not be symmetrical; they will differ quantitatively on the two sides, and in some cases even qualitatively since one isomer and not the other may form a compound with the solvent (Fig. 13-32). The dissymmetry of the diagram of Fig. 13-31(c) with an active solvent may be such that the racemic compound may be incongruently soluble.

If the isomers d and l suffer instantaneous racemization in the inactive solvent, in which the diagram is always symmetrical, the system is no longer ternary but binary, for the only solid possible is racemic and congruently soluble as a single phase whether physically homogeneous or not. If the

racemization proceeds with finite rate, the system is pseudoternary. When the solvent is optically active, the instantaneous racemization of the *d* and *l* isomers of the solutes in the liquid phase again gives a binary system, despite the dissymmetry of the phase diagram. The composition of the unsaturated liquid will always lie on the line Cl_x , and at saturation it will precipitate the *l* form in Fig. 13-32(a) and the diastereo-isomer, or the compound D, in Fig. 13-32(b). But as the solids are precipitated the composition of the saturated solution cannot move from point l_x , during isothermal evaporation of the solvent, for example, and the other possible solids will never be formed, in equilibrium relations. The point l_x then becomes the

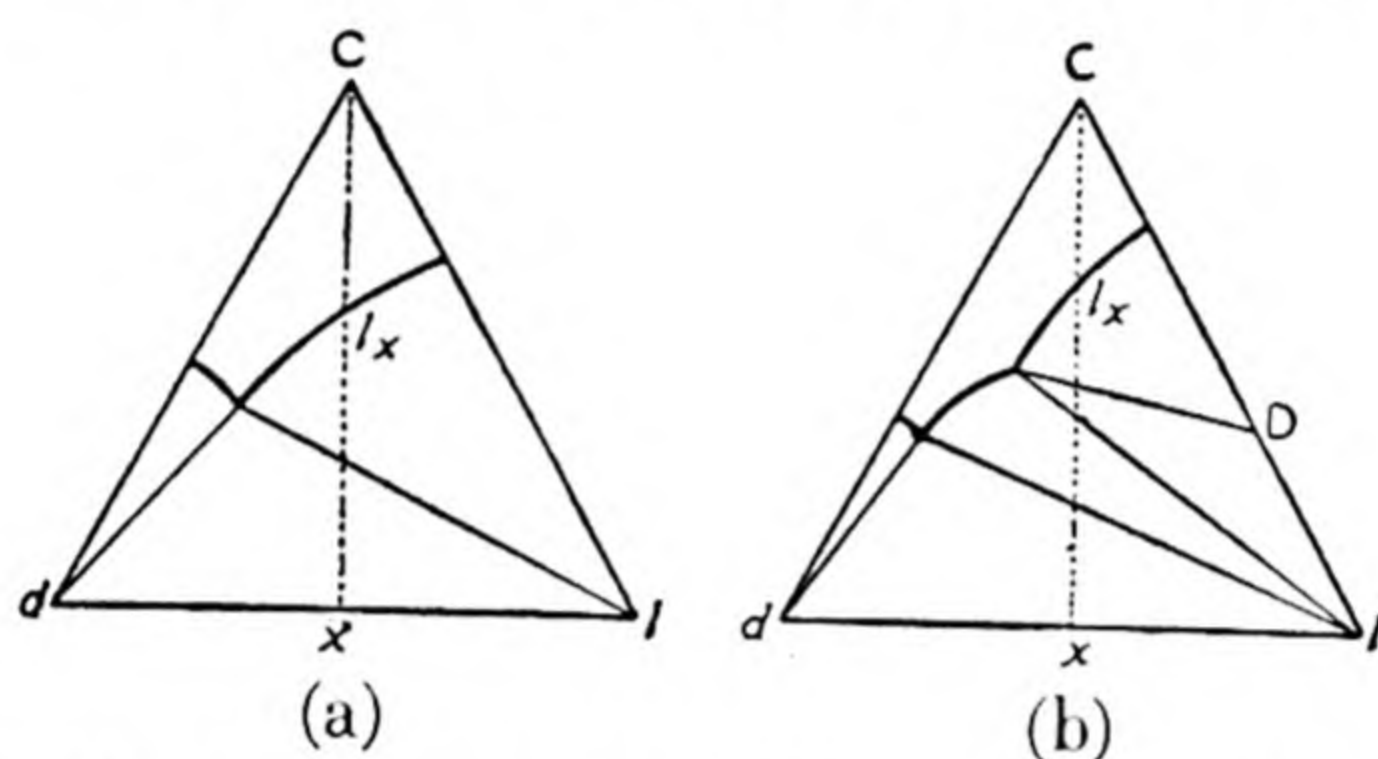


FIG. 13-32. Optical isomers with optically active solvent.

“natural” solubility of the solute in the solvent C — comparable with the natural freezing point of pseudobinary systems, discussed in Chapter VI; in Fig. 13-32(a) the solid phase is unsolvated, whereas in Fig. 13-32(b) it is solvated. If the racemization proceeds at a finite rate, such a system is then pseudoternary. If the solute forms a racemic compound congruently soluble in the solvent, the natural solubility will be a point on the solubility curve of the compound; but if the racemic compound is incongruently soluble in the active solvent, the natural solubility will be a point on the solubility curve of one of the isomers, which will be the “natural solid form” of the pseudoternary system.

As discussed in Chapter VII-H, the optical isomers *d* and *l* are merely special cases of pseudocomponents, differing from the general case in that the two forms are present in 1:1 proportions at complete equilibrium. The internal equilibrium is, therefore, in general not the simple straight line Cx , and does not intersect the base at its mid-point. The general case is discussed by Smits.³⁴

The ternary system consisting of water and rubidium *d*- and *l*-tartrates involves a racemic compound which is stable in contact with solution up to the temperature 40°, point P of the schematic polythermal projection, Fig. 13-33(a); above this temperature the isotherm must change from the type

³⁴ A. Smits, Ref. R.

of Fig. 13-31(c) to 13-31(a). The transition point P must be of the nature of that of Fig. 12-45(b) but in a symmetrical diagram. The composition of the compound D is 1:1 and at the same point of the composition plane as the eutectic e_3 of the binary system of the d and l forms. The isotherm

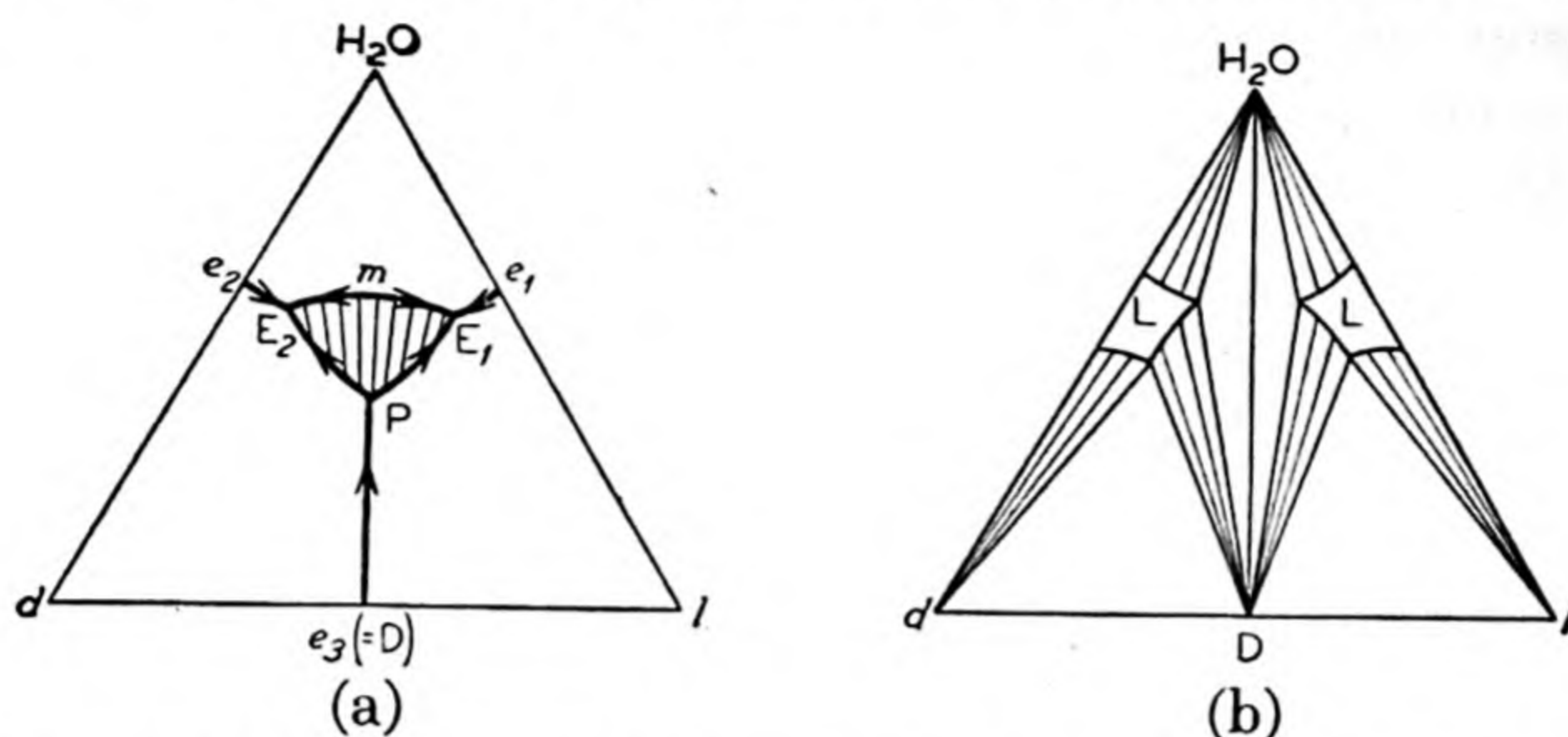


FIG. 13-33. System rubidium tartrate — water (schematic)

would be as in Fig. 13-31(c) between the transition point P (40°) and T_m ; above P, as in Fig. 13-31(a); below T_m , but above the eutectics E_1 and E_2 , which are at the same temperature, as in Fig. 13-33(b); (T_m must be $< 0^\circ$). The diagrams are hypothetical and schematic, but the temperature of P is known from the plot of the concentration of the solution k of Fig. 13-31(a and c) as function of T , shown as Fig. 13-34.³⁵ Below P, the solution k is saturated with the racemic compound and supersaturated with the racemic

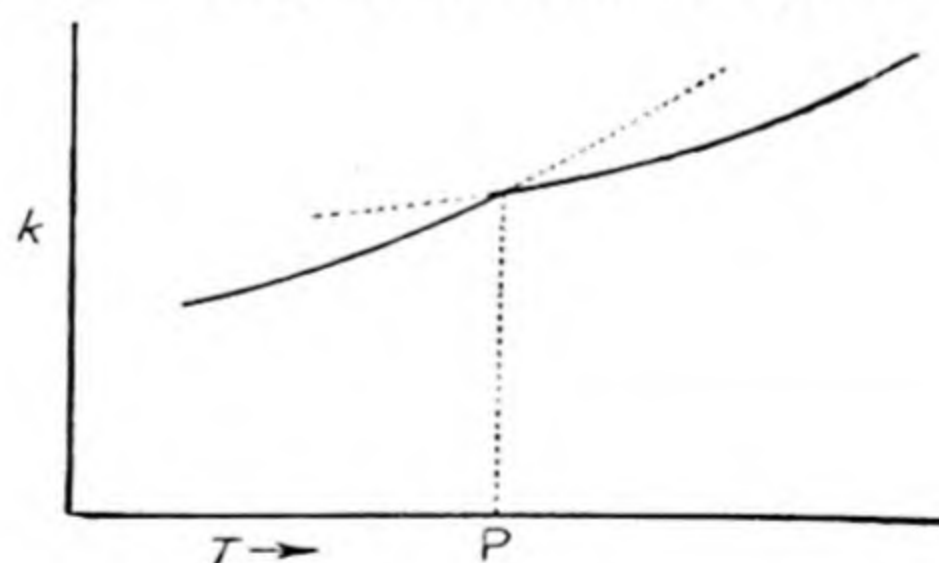


FIG. 13-34. Determination of temperature of transition point P.

mixture, while above P it is saturated with the mixture and supersaturated with the compound. The two solubility curves therefore cross at the temperature of P.

In connection with Fig. 13-33 we may mention a method given by Bruni³⁶ for the investigation of the relations of optical isomers. If the eutectic curve $e_1E_1mE_2e_2$ is projected on the vertical T/c plane of the binary system $d-l$, the resulting diagram, as in Fig. 13-4(a), indicates the formation of a binary compound. If the third component, or the "solvent," is now changed to one of higher melting point, the curve E_1mE_2 becomes smaller.

³⁵ J. H. van't Hoff and W. Müller, *Ber.*, **31**, 2206 (1898).

³⁶ G. Bruni, *Att. R. Accad. Lincei*, [5], **8-I**, 332 (1899); *Gazz. chim. Ital.*, **30-I**, 35 (1900).

If the third component has a high enough melting point, this curve disappears, leaving either the type seen in Fig. 13-2, showing that the optical isomers give a simple eutectic melting point diagram, or a continuous curve, as would be the case in Fig. 12-6, if the optical isomers form a continuous solid solution at their melting points. In this way, by using the substances naphthalene, phenanthrene, benzoin, and anthracene as third component, Adriani³⁷ established that the *d*- and *l*-camphoroximes form a compound which decomposes above 103° to a solid solution.

The general system consisting of water and sodium and ammonium tartrates (meso-tartrates being excluded) is quaternary, since the solutes are related in the reciprocal fashion $d\text{-Na}_2\text{T} + l\text{-(NH}_4)_2\text{T} \rightleftharpoons l\text{-Na}_2\text{T} + d\text{-(NH}_4)_2\text{T}$; the symbol T is here used for the tartrate radical. In the range from room temperature to above 35° the solid phases encountered, in addition to the four individual isomers, are the racemic compounds *r*-Na₂T (I) and *r*-(NH₄)₂T (II), the active double salts (optical isomers) *d*-NaNH₄T (III) and *l*-NaNH₄T (IV), and the racemic double salt *r*-NaNH₄T (V). In the completely racemized system, therefore, we may expect ternary behavior, with any of the inactive solids I, II, and V as sole solid phases, or various inactive mixtures of solid phases. Between 27° and 35° the racemic double salt V is the stable solid phase if the solution contains the sodium and the ammonium compounds in equivalent proportions. Above 35° it breaks down to a mixture of the racemic compounds I and II, whereas below 27° it decomposes to a mixture of the optically active double salts III and IV, the crystals first separated as enantiomorphs by Pasteur. The reaction at the transition point of 27°³⁸ is $d\text{-NaNH}_4\text{T} \cdot 4\text{H}_2\text{O} + l\text{-NaNH}_4\text{T} \cdot 4\text{H}_2\text{O} + \text{cals.} \rightleftharpoons 2\text{ } r\text{-NaNH}_4\text{T} \cdot \text{H}_2\text{O} + 6\text{H}_2\text{O}$. With the sodium and ammonium compounds always present in equivalent proportions and in the temperature range in which the only solid phases involved are III, IV, and V, the system may be considered ternary, the isotherm being of the type of Fig. 13-31(a) below, and Fig. 13-31(c) above, 27°. This transition point, finally, would be of the type of point P in Fig. 12-43, but in a symmetrical diagram.

³⁷ J. H. Adriani, *Z. phys. Chem.*, **36**, 168 (1901).

³⁸ J. H. van't Hoff and C. M. van Deventer, *Z. phys. Chem.*, **1**, 165 (1887).

Chapter XIV Freezing Point Equilibria Involving Two or Three Liquid Phases

A. Two Liquid Phases

If the liquid miscibility gap, discussed in Chapter X, Section C, impinges on the solidification surfaces, freezing point or solubility equilibria arise which involve two liquids. The intersection of a liquid *MG* with one of the crystallization surfaces, or the presence of a 2-liquid area on a crystallization field, produces a 3-phase isobarically univariant equilibrium of solid and two liquids. The solid may be a component or a compound. If it is a pure solid, as will be assumed in this chapter, then this 3-phase equilibrium appears as a pair of liquid curves on the polythermal projection of the system on the composition plane, since one of the phases is merely the point representing the pure solid. As a 3-phase equilibrium, it is a space in the T/c prism, generated by an isothermal 3-phase triangle, one corner of which is the fixed solid phase while the other two are the compositions of the conjugate liquids simultaneously saturated with that solid.

1. Isothermal Relations

If the *MG* intersects the crystallization surface of the high-melting component B, an isotherm above the melting points of A and C will appear as in Fig. 14-1. In Fig. 14-1(a) the solubility curve of B, normally running from *a* to *d*, is interrupted by the isothermal binodal curve of the *MG* between *b* and *c*. On the curves *ab* and *cd* the liquid is saturated as usual with solid B, and the curve *bc* is the binodal curve, a 2-phase region of conjugate liquids with *k* as the critical solution point or plait point for this temperature. All compositions in the triangle I consist at equilibrium of the three phases, liquids *b* and *c*, and solid B, the proportions of the phases being calculated as explained in Chapter X for any such isothermally invariant triangle. Although the liquid components A and C are completely miscible at this temperature, the addition of B to mixtures of A and C within the range *xy* (*y* being the extension of the line *tB* tangent to the binodal curve) leads not to saturation with solid B but first to the formation of a 2-liquid system, when the concentration of B reaches a point on the binodal curve. More commonly, the relations at *c* would be similar to those at *b*, without such a tangent, *tB*, cutting the solubility curve *cd*. At any rate, while the

total composition is in the binodal region, the tie-line through the total composition gives, as usual, the compositions and proportions of the conjugate liquids. When the line bc is reached, as at point z , the solid B is simply left in excess. If the proportions of A and C lie between t and c , then the second liquid phase disappears again when addition of B brings the total composition to the curve tc , finally reaching saturation with solid B on the curve cd , for a single liquid + B.¹

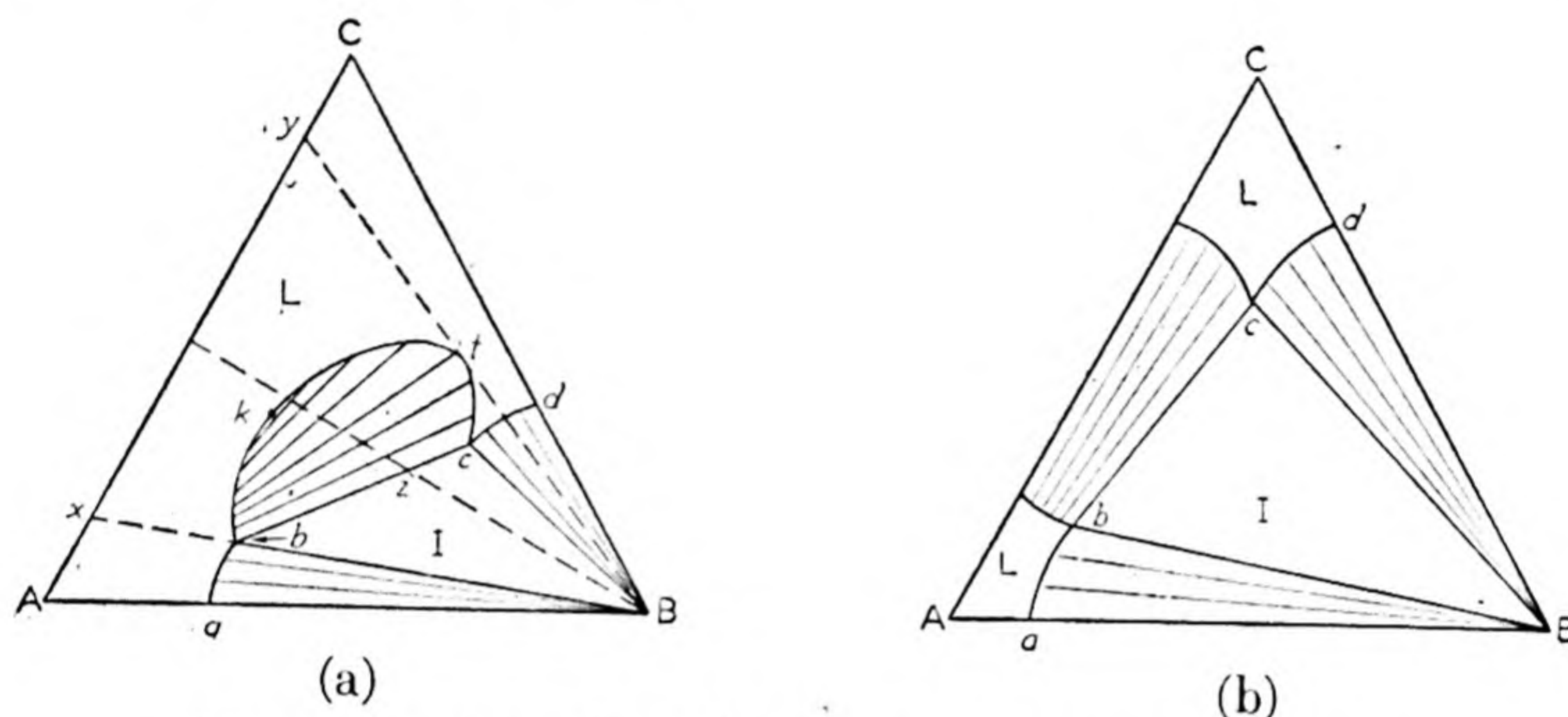


FIG. 14-1. Liquid miscibility gap and one solid phase.

If, by change of T , the binodal curve reaches the side AC, it touches it at the point k , which is then the upper or lower critical solution point of the liquids A and C, leading further to the isotherm of Fig. 14-1(b). The isotherm may also show a binodal region based on the binary system A-C but not extending to an intersection with the solubility curve of solid B. The relations are then simple, involving no equilibrium of solid and two liquids.²

The slant of the tie-line bc of Fig. 14-1(a) depends essentially on the difference between the solubility of B in A and its solubility in C. If the solubility of B in A is very small, but large in C, then, with point b very close to A, it is possible to "salt out" A from a solution of A + C, by addition of the salt B. Fig. 14-2 represents, schematically, the system alcohol (A)- K_2CO_3 (B)-water(C) at room temperature.³ Addition of the salt to aqueous alcohol causes the liquid to split into two layers, but when the line cd is reached the saturating solid phase is the sesquihydrate. The conjugate solutions c and d are saturated with this solid phase, with the interrupted solubility curve bc and de , the latter curve de being extremely short at room temperature. But on the absolute alcohol side the saturating solid phase

¹ For many examples of such simple relations, see P. M. Ginnings and M. Dees, *J. Am. Chem. Soc.*, **57**, 1038 (1935); other articles by Ginnings are there mentioned.

² See, for example, the system benzene-propylene glycol-sodium oleate at 20°; S. R. Palit and J. W. McBain, *Ind. Eng. Chem.*, **38**, 741 (1946).

³ G. B. Frankforter and F. C. Frary, *J. Phys. Chem.*, **17**, 402 (1913).

must be the anhydrous salt, with the solubility curve ab . Point c at room temperature (23° – 26°) contains $\sim 91\%$ alcohol and 0.1% salt. Point b , with $\sim 0.5\%$ water and 1.6% salt, is experimentally hardly distinguishable from point a . If solid K_2CO_3 is added to aqueous alcohol until an excess of solid hydrate is present (triangle I), the alcohol layer is solution c , with 91% alcohol. If the salt is added until the anhydrous salt is present in excess, together with the hydrate (triangle II), the (single) supernatant liquid is solution b , with 99.5% alcohol, not counting the dissolved salt. Similar relations hold in the system KF –alcohol– H_2O , the hydrate being $\text{KF}\cdot 2\text{H}_2\text{O}$.³ The “salting out” of the alcohol may be said to be brought about by two effects: the splitting of the liquid phase and the formation of the solid hydrate.⁴

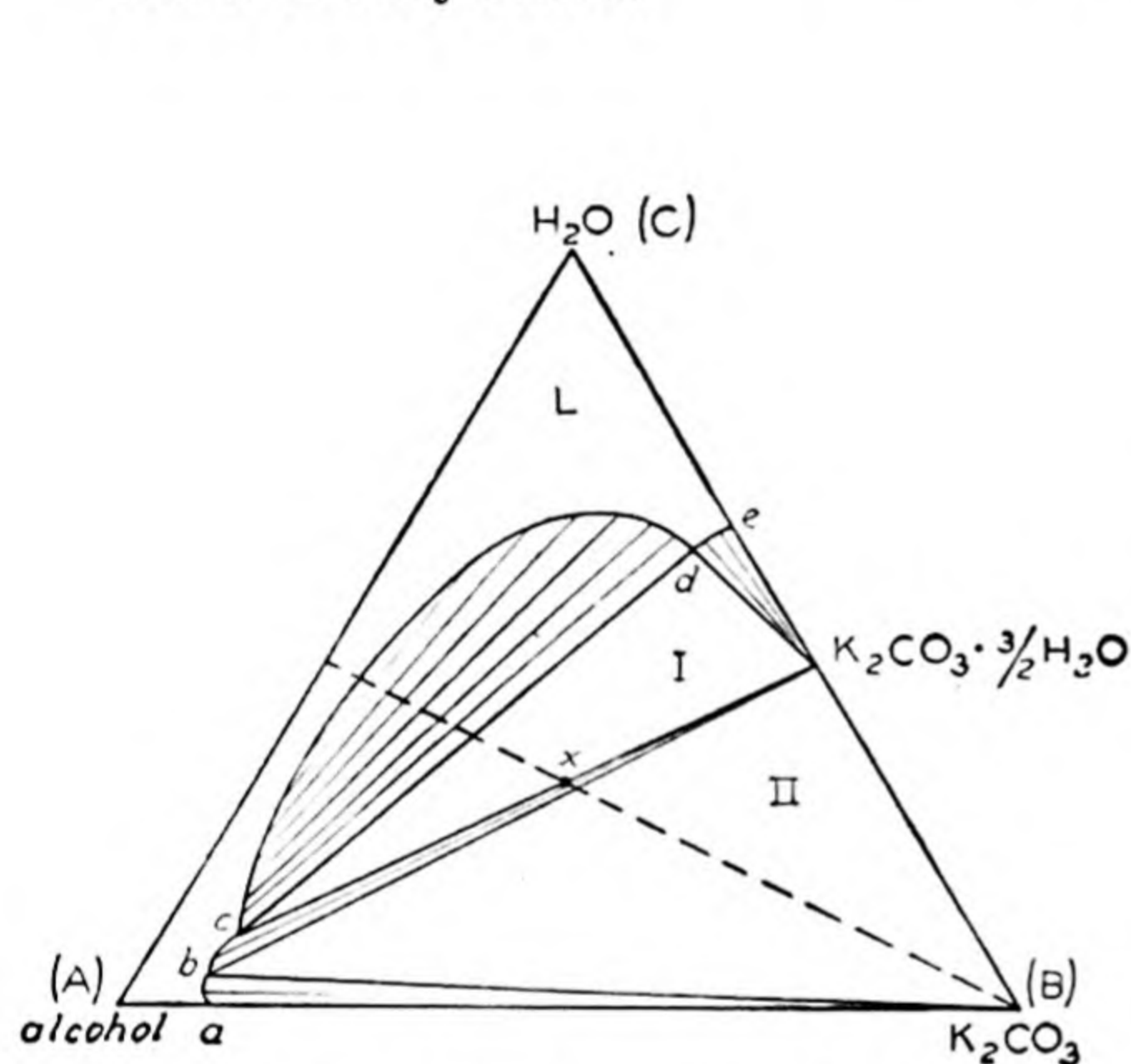


FIG. 14-2. System alcohol– K_2CO_3 –water, schematic isotherm.

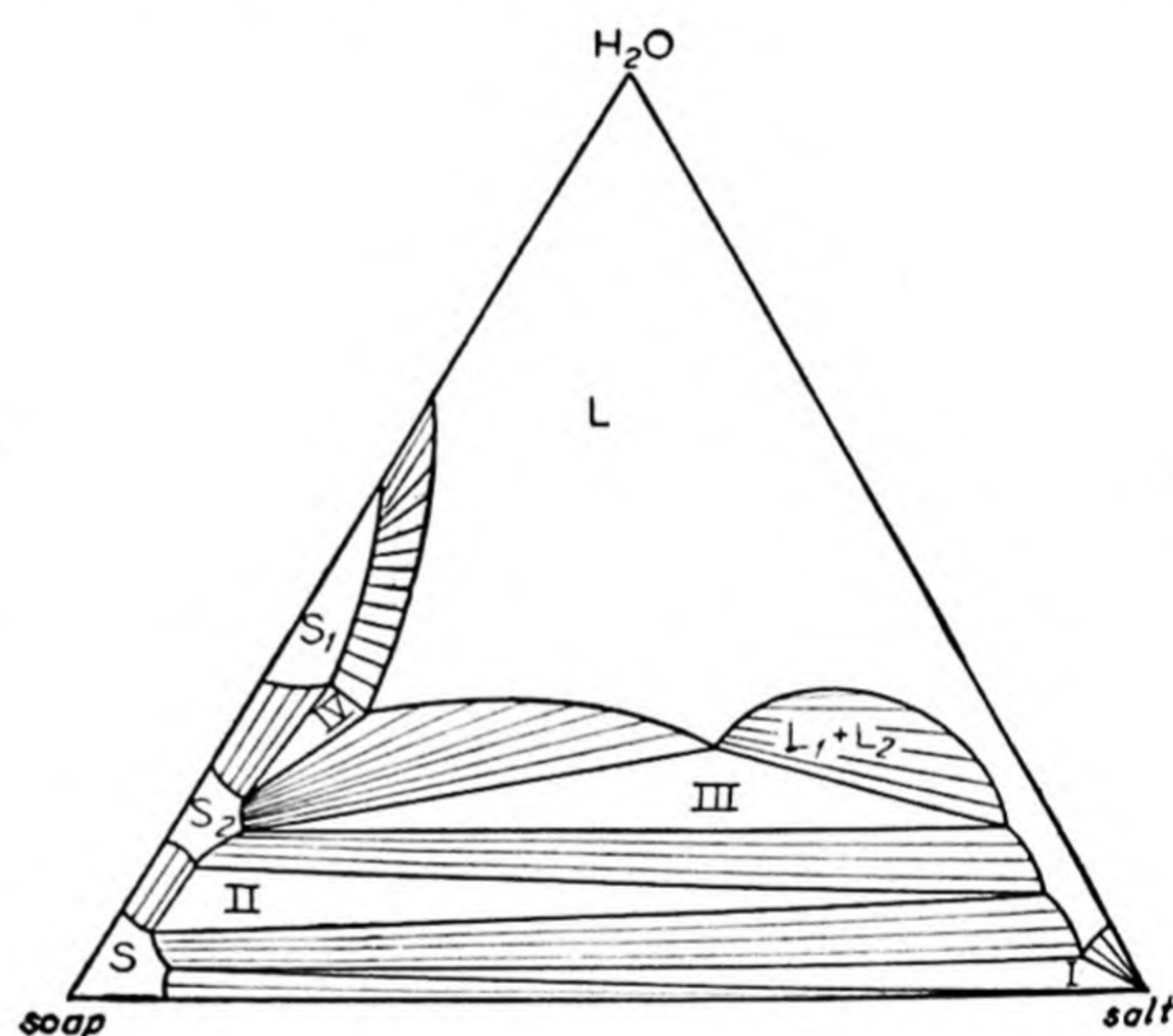


FIG. 14-3. System soap–salt–water, schematic isotherm.

Fig. 14-2 also represents schematically the 60° isotherm of the system ammonia (A)– NaOH (B)–water(C), under a vapor pressure varying between 260 and 320 pounds per square inch,⁵ with the compound $\text{NaOH}\cdot\text{H}_2\text{O}$ in place of $\text{K}_2\text{CO}_3\cdot 3/2\text{H}_2\text{O}$. Fig. 14-3 is a schematic isotherm for the system soap–water–salt.⁶ The binary side soap–water is to be compared with Fig. 7-46, at a temperature between E_1 and E'_2 ; the “solid phases” are therefore some liquid crystalline form of soap (S), neat soap (S_2), and middle soap (S_1), all presumably variable and ternary in nature. The solubility curve of neat soap is seen to be interrupted by a 2-liquid binodal region,

⁴ For a practical example, see H. P. Meissner and C. A. Stokes, *Ind. Eng. Chem.*, **36**, 816 (1944).

⁵ F. D. Ayres, *J. Phys. Chem.*, **49**, 366 (1945).

⁶ J. W. McBain, R. D. Vold and M. J. Vold, *J. Am. Chem. Soc.*, **60**, 1866 (1938).

and there are four isothermally invariant triangular regions: I for salt + liquid + soap, II for soap + liquid + neat soap, III for neat soap + two liquids, and IV for neat soap + liquid + middle soap.

2. The "Intersection Curve," or the Equilibrium Solid + Two Liquids

If the MG impinging on the crystallization surface of B does not extend to any boundary of the B field, as in Fig. 14-4, the intersection curve, representing the equilibrium between conjugate solutions saturated with solid, will be closed, with two critical solution points, K and K'. At these points the consolute curve $L_1 = L_2$, or K_1K_2 , of Figs. 12, 15, 16 and 17 of Chapter X, meets the crystallization surface for the equilibrium of L and B. These points will be at different temperatures, because of the curvature of the

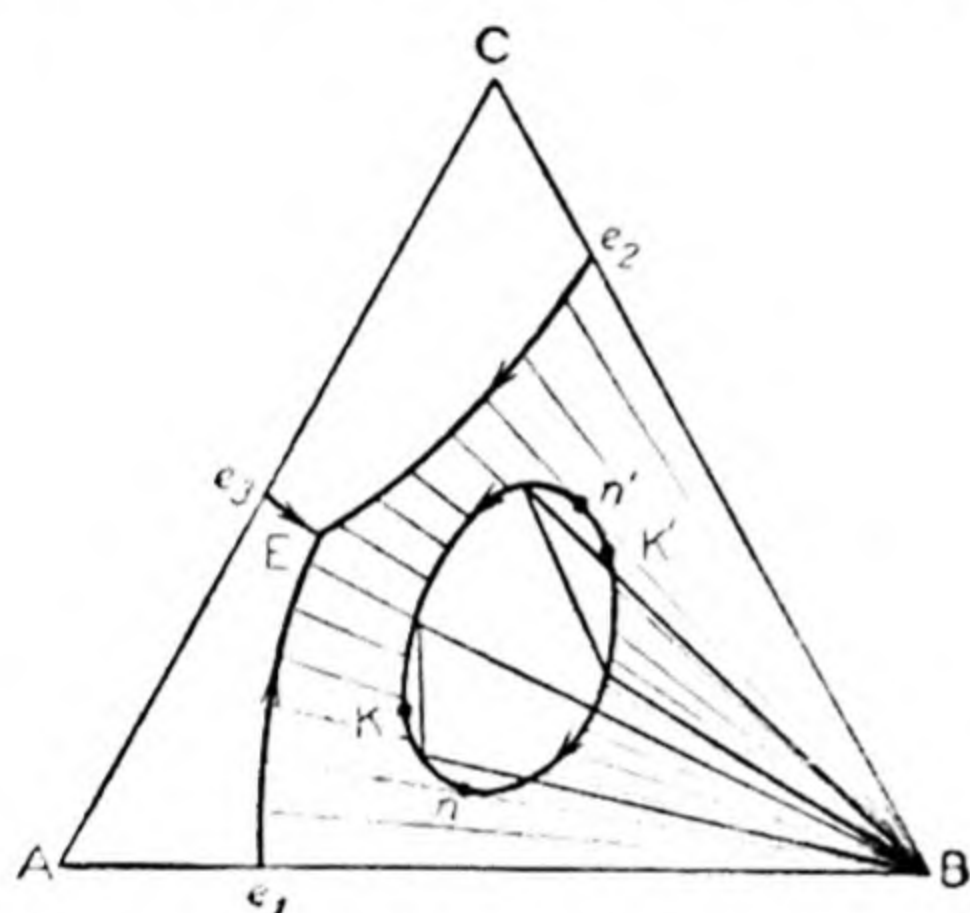


FIG. 14-4. Closed intersection curve, l_1l_2B .

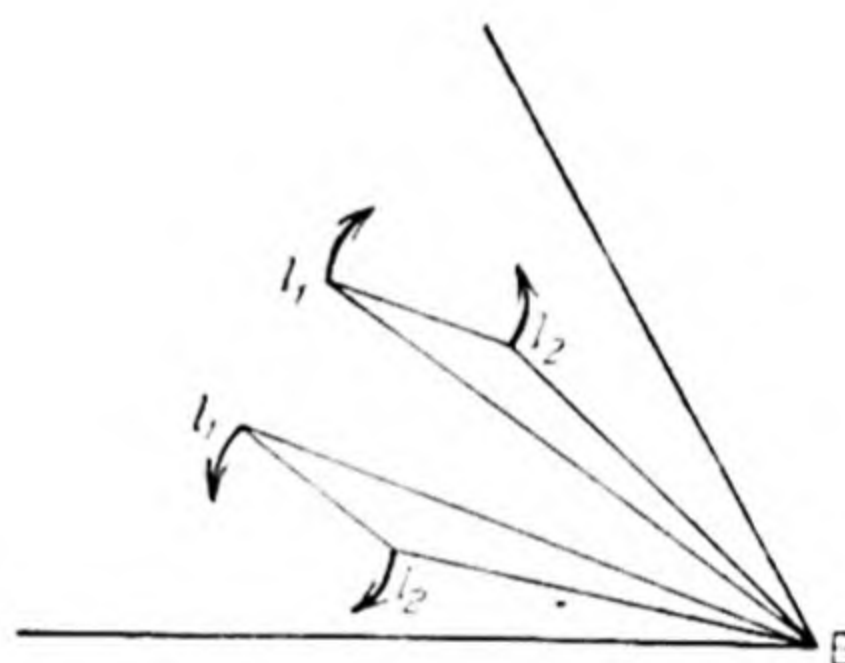


FIG. 14-5. Course of liquid curves in polythermal projection.

crystallization surface of B, and there may be a maximum or minimum temperature for the equilibrium l_1l_2B between them. The 3-phase triangle (isothermal) l_1l_2B , generating this closed curve with its l_1 and l_2 corners, collapses to a line at each critical solution point, where l_1 and l_2 become identical while saturated with B. The arrangement of the points l_1 , l_2 , and B of the 3-phase triangle is related to the direction of falling T on the intersection curve, since the liquidus surface (namely, the crystallization surface) is always above the solidus in temperature. Thus we have Fig. 14-5, in which the arrows, as usual, show the direction of falling T . Hence, if n and n' in Fig. 14-4 are points at which the intersection curve is tangent to tie-lines from B, then K' is a point of maximum T on the curve, and K a minimum.

If the MG is stable above the crystallization surface of B, so that it may be said merely to impinge upon this surface, then an isotherm above the maximum K' of Fig. 14-4 shows a closed MG not intersecting the solubility curve of B, as in Fig. 14-6(a). The points k and k' here represent plait points of unsaturated conjugate solutions at the T of each particular

isotherm. With falling T the isothermal plait point k' comes to touch the solubility curve at the temperature K' , and between K' and K the isotherm has the appearance of Fig. 14-6(b), with part of the MG submerged or metastable. With continued fall of T , the second plait point k also becomes

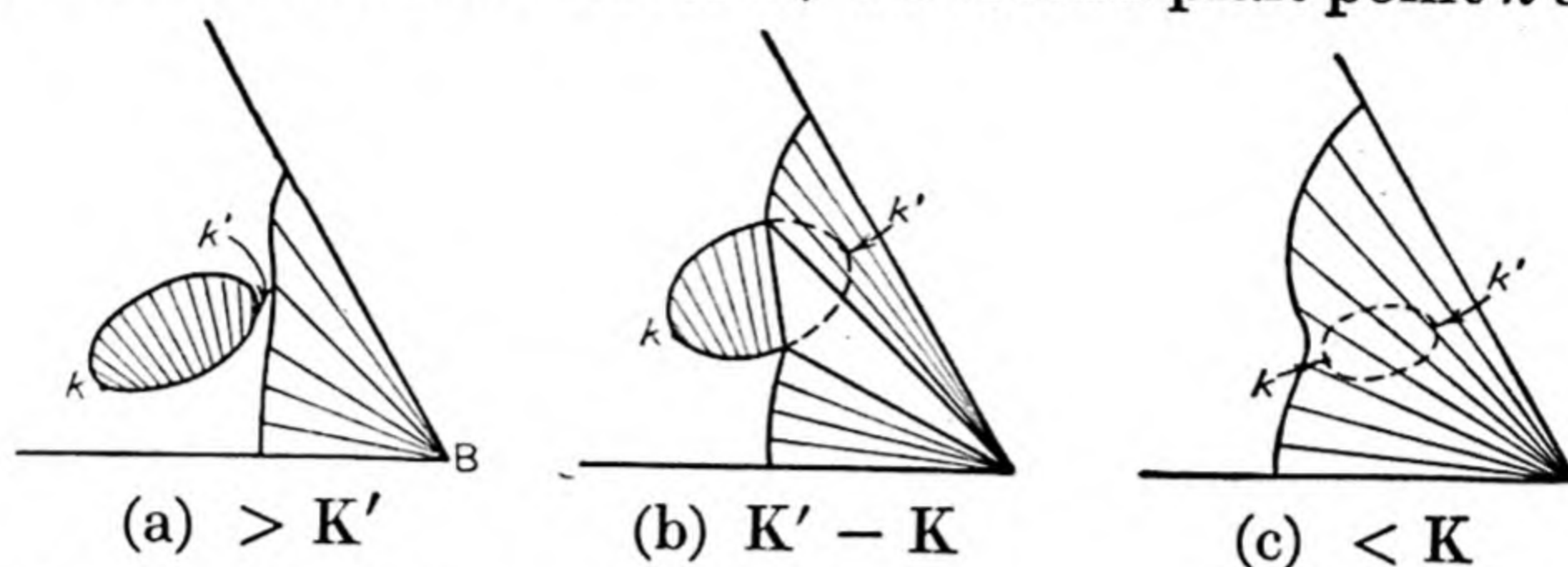


FIG. 14-6. Submerging of MG ; isotherms of Fig. 14-4.

submerged at point K of Fig. 14-4, giving the isotherm of Fig. 14-6(c) in which the MG is all metastable. It is also possible for the consolute curve $L_1 = L_2$ to fall continuously in temperature from K' to K in Fig. 14-4. Then the isotherms both above K' and below K would be of the type of Fig. 14-6(c), with no part of the MG stable, and between K' and K the isotherm would be schematically Fig. 14-6(b), so that only the plait point k would be involved both at K' and at K . In this case the MG may be described as merely a bubble on the crystallization surface of B , the maximum temperature of the bubble being submerged beneath this surface. The

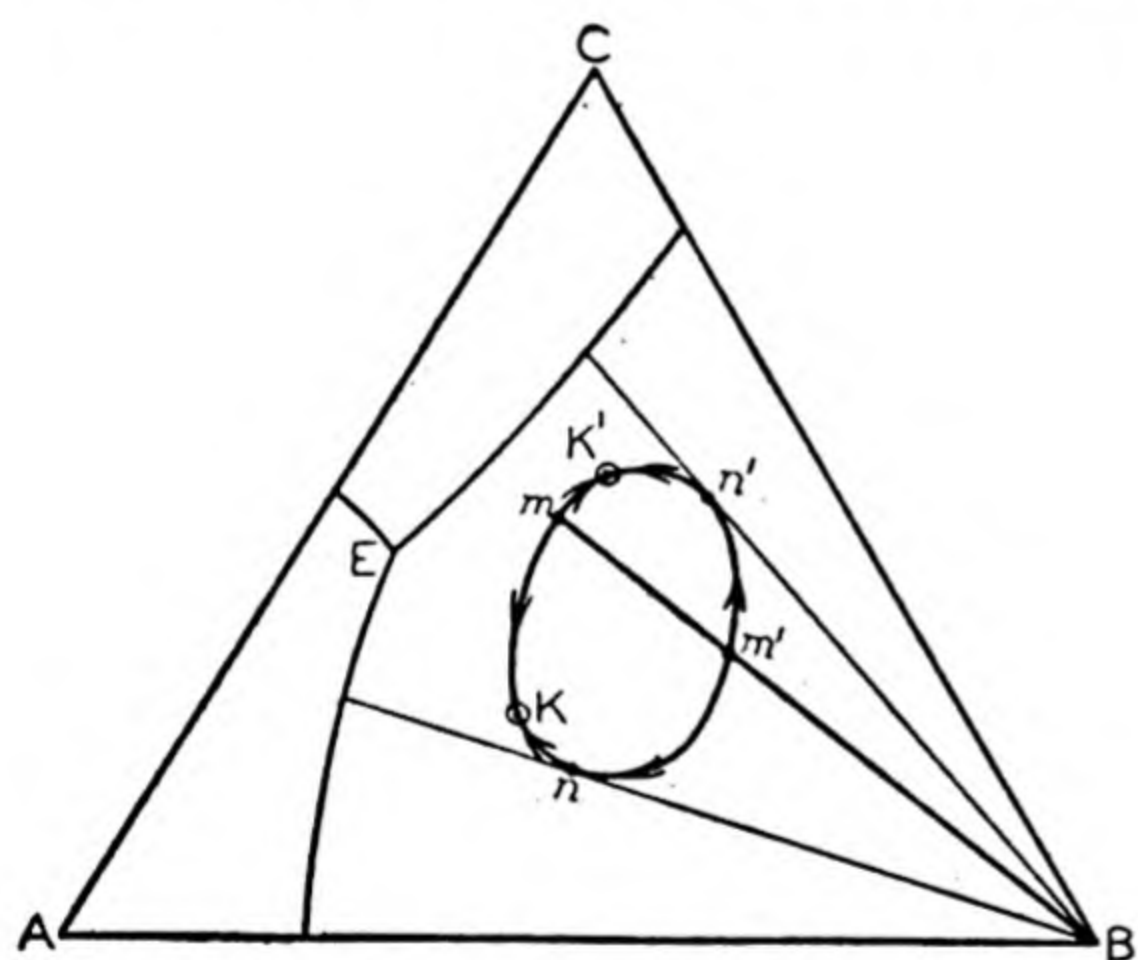


FIG. 14-7. Closed intersection curve, with temperature maximum.

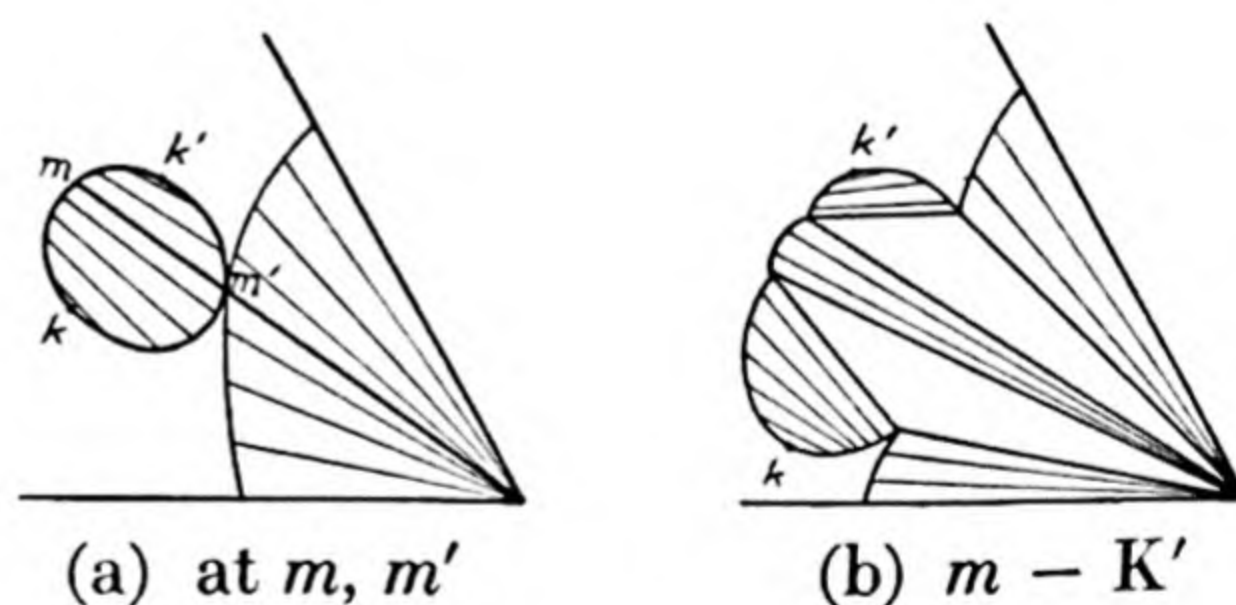


FIG. 14-8. Isotherms of Fig. 14-7.

critical solution points just described in connection with Figs. 14-4 and 14-6 are (isobaric) singular points of type k , and may be compared with those discussed under Fig. 10-19.

If the contact between binodal curve and solubility curve, occurring between Figs. 14-6(a) and 14-6(b), is not at one of the plait points (k, k'), we have Figs. 14-7 and 14-8. In the polythermal projection (Fig. 14-7)

K and K' are now both on the AC side of the tangency points n and n' , and they are both minima of the intersection curve. At the maximum between K and K' , the 3-phase triangle becomes the straight line $mm'B$. With $K' > K$ in temperature, the isotherms of Fig. 14-8 are followed by Figs. 14-6(b) and (c).

Given an unusual concavity of the crystallization surface with respect to the approaching MG , the minimum temperature of the intersection curve may lie between K and K' as maxima. The isotherms and polythermal projection now appear as in Figs. 14-9 and 14-10. Here both the critical solution points K and K' , for the equilibrium l_1l_2B , are on the B side of the points n, n' ; they are both maxima of the intersection curve, and the minimum is the colinear equilibrium $mm'B$.⁷ The colinear equilibria $mm'B$ of Figs. 14-7 and 14-9 are (isobaric) singular points of type m , as described under Figs. 10-21 and 10-22, respectively.

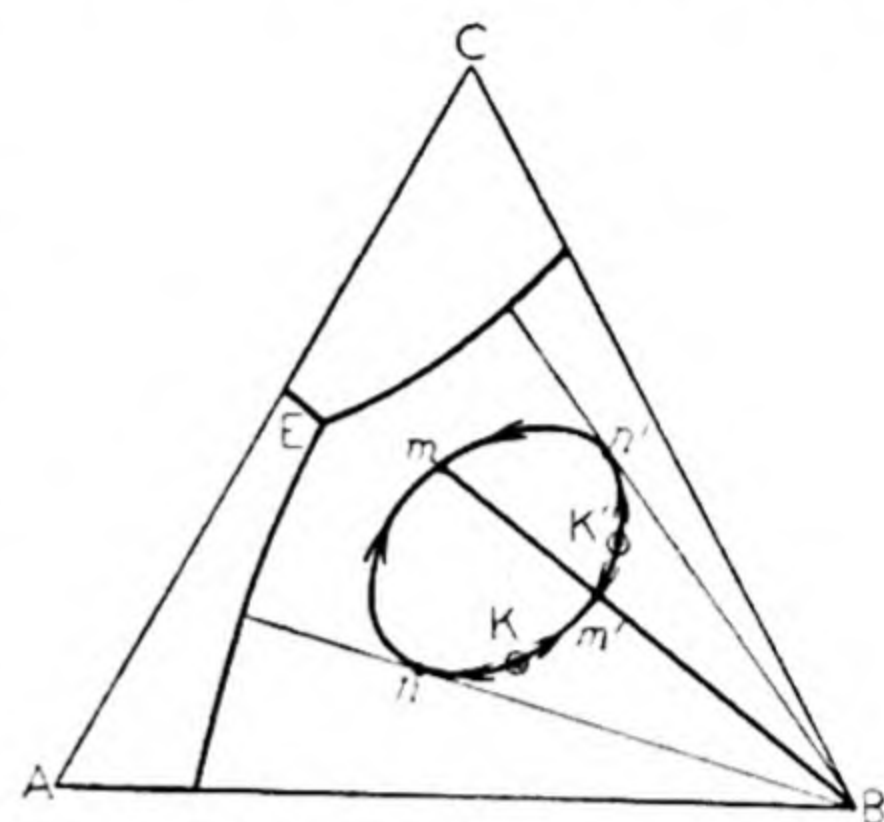


FIG. 14-9. Closed intersection curve, with temperature minimum.

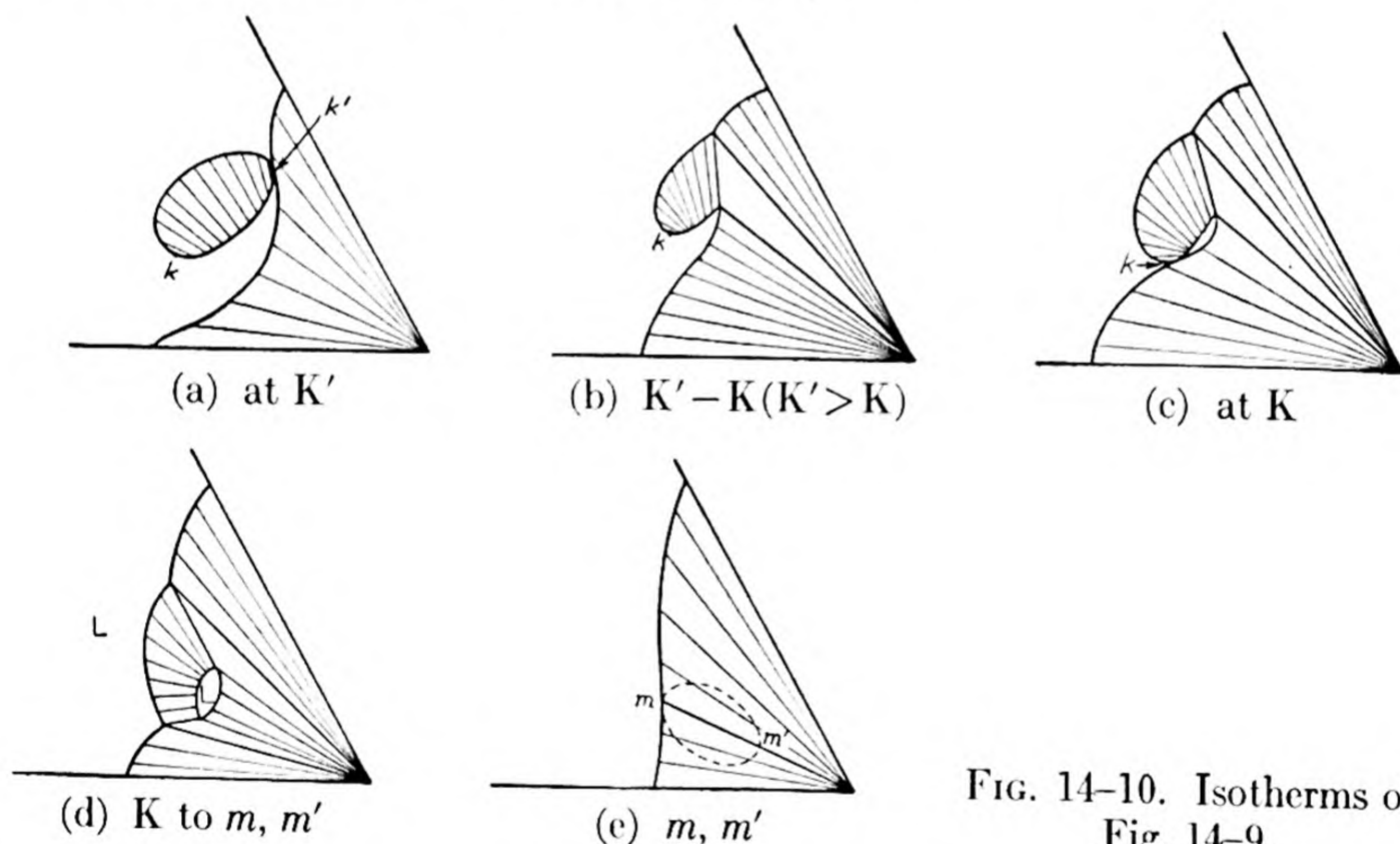


FIG. 14-10. Isotherms of Fig. 14-9.

The intersection curve, shown as a closed curve for the cases of Figs. 14-4, 14-7, and 14-9, may also extend to a binary side, to start or end, therefore, at a binary 3-phase (isobarically) invariant point; this is the case for the equilibrium l_1l_2B in Fig. 14-11. In Fig. 14-11(a) the 3-phase system

⁷ Some of the relations discussed under Figs. 14-6 to 14-10 may be seen as parts of the systems AgClO_4 -benzene-water and AgClO_4 -toluene-water studied by A. E. Hill, *J. Am. Chem. Soc.*, 44, 1163 (1922), and A. E. Hill and F. W. Miller, *ibid.*, 47, 2702 (1925).

of the intersection curve originates as the line abB in the A-B system and travels on the B field, with falling T , to the critical solution point K. In Fig. 14-11(b) the intersection curve extends to a similar binary invariant on the CB side. Depending on the shape of the crystallization surface involved, the intersection curve may still have a ternary maximum or minimum, whatever the nature of its terminations, that is, either in Fig. 14-11(a) or in Fig. 14-11(b). The maximum or minimum will be distinguished by the fact that the phases l_1 , l_2 , and B there become colinear.

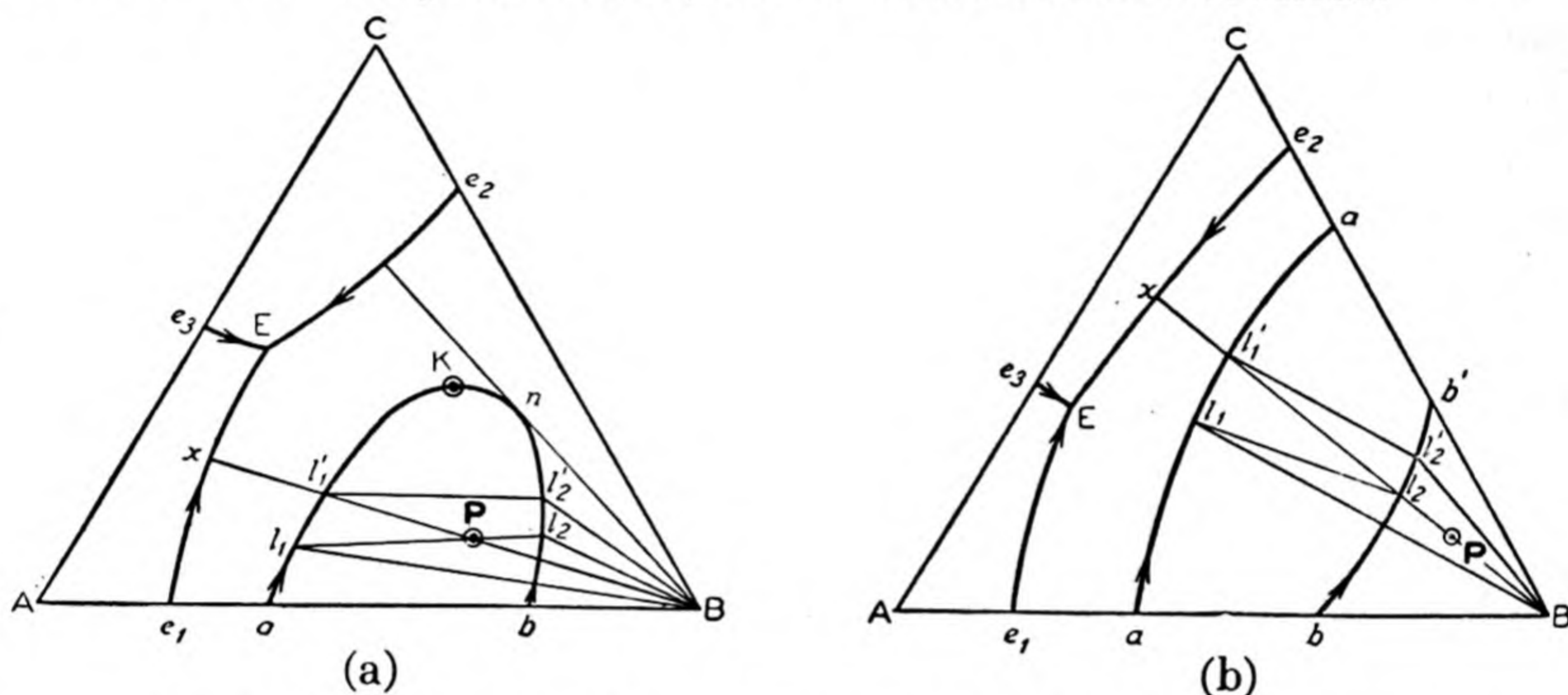


FIG. 14-11. Intersection curve extending to binary systems.

Ternary liquids with compositions on the AC side of the points of tangency in Figs. 14-4, 14-7, 14-9 and 14-11(a), or on the AC side of the curve aa' of Fig. 14-11(b), behave in the usual way on cooling, as explained in Chapter XII, reaching the eutectic E and leaving a mixture of the three solid components. But all ternary compositions, anywhere in the composition triangle, must similarly solidify to a mixture of A, B, and C solids, and must therefore all reach E. All compositions other than those mentioned, therefore, merely first pass, temporarily, through the 3-phase equilibrium state, l_1l_2B . If the original composition falls within the intersection curve or curves, it is a 2-liquid system when solid first appears. When complex P (a 2-liquid system) in Fig. 14-11(a) is cooled, the liquids have the compositions l_1 and l_2 when solid B first appears. The temperature at which this occurs can be determined from various vertical projections of the T/c prism, as explained under Figs. 2 to 5 of Chapter XIII. As T falls, the liquids proceed along the intersection curve, converging toward point K, and the relative amounts of the three phases may be calculated from the position of P in the 3-phase triangle l_1l_2B for any given T . But a point will be reached when P is swept by the l_1B tie-line of this triangle. At this temperature the l_2 phase will have disappeared, with composition l'_2 , leaving $l'_1 + B$, whereupon the liquid, still precipitating B, proceeds, in the

usual way, on the straight line crystallization path BP'_1 to point x on the eutectic curve e_1E . Similar relations hold for composition P in Fig. 14-11(b). This reaches the crystallization surface as a single liquid phase and, while precipitating B , moves on the straight line BP to the intersection curve for the equilibrium l_1l_2B . When it reaches the point l_2 on the curve bb' (B-rich liquid phase), liquid of composition l_1 appears, on the curve aa' . The two liquids then proceed toward the CB side with further cooling, but, when the tie-line l_1B comes to include the point P , the original liquid phase will have been consumed, with final composition l'_2 , leaving $l'_1 + B$. Now the liquid proceeds on the line BP'_1 to the point x on the eutectic curve e_2E , and finally to E .

These relations hold just as well, of course, if the curve is completely closed, as in Figs. 14-4, 14-7, and 14-9. The critical solution points K and K' are reached, for equilibrium, only if the composition P lies on the line BK or BK' .

Fig. 14-11(a) is illustrated by the system $Pb(A)-Zn(B)-Cd(C)$ ⁸ and apparently also by the system $alcohol(A)-KNO_3(B)-water(C)$.⁹ The system $Ag(A)-Ni(B)-Cu(C)$ ¹⁰ differs from Fig. 14-11(a) only in that Ni and Cu form a continuous solid solution (ascendant) so that there is a simple eutectic curve running smoothly and continuously, with falling temperature, from e_1 to e_3 ; the two solids involved are not pure but actually ternary solid solutions, so that were it not for the binodal curve the polythermal projection would be schematically similar to Fig. 11-9(a).

3. Invariant Points; Two Solids and Two Liquids

If the intersection curve reaches one of the eutectic curves (e_1E , for example), there will be a 4-phase invariant point, Q , involving the phases L_1 , L_2 , B , and A ; the intersection curve then continues into the A field, to end either at a critical solution point involving two liquids and solid A , or at one of the binary sides, AB or AC . Hence there are many possible diagrams, some of which are shown in Fig. 14-12 in polythermal projection. For some examples we may mention the systems $Fe-Fe_3C-FeS$ and $Fe-Fe_3P-FeS$ ¹¹ for Fig. 14-12(b); $phenol(A)-water(B)-triethylamine(C)$ for Fig. 14-12(c);¹² $ether(A)-succinic nitrile(B)-water(C)$ for Fig. 14-12(e);¹³ and $benzoic acid(A)-succinic nitrile(B)-water(C)$ for Fig. 14-12(g).¹⁴

⁸ M. Cook, *J. Inst. Metals*, **31**, 297 (1924).

⁹ N. Dodge and L. C. Graton, *J. Phys. Chem.*, **2**, 498 (1898).

¹⁰ W. Guertler and A. Bergman, *Z. Metallkde*, **25**, 53 (1933).

¹¹ R. Vogel (Ref. V), pp. 541-542; some binary solid solution is also involved.

¹² P. A. Meerburg, *Z. phys. Chem.*, **40**, 641 (1902); phenol hemihydrate is here ignored.

¹³ F. A. H. Schreinemakers, *ibid.*, **25**, 543 (1898).

¹⁴ F. A. H. Schreinemakers, *ibid.*, **26**, 237 (1898).

In Fig. 14-12(a), the MG lies across the eutectic curve e_1E , ending at a critical solution point in each of the adjacent crystallization fields, and these points are both maxima of the intersection curve, the minimum of which is on the eutectic curve. This minimum is the invariant point Q , for the

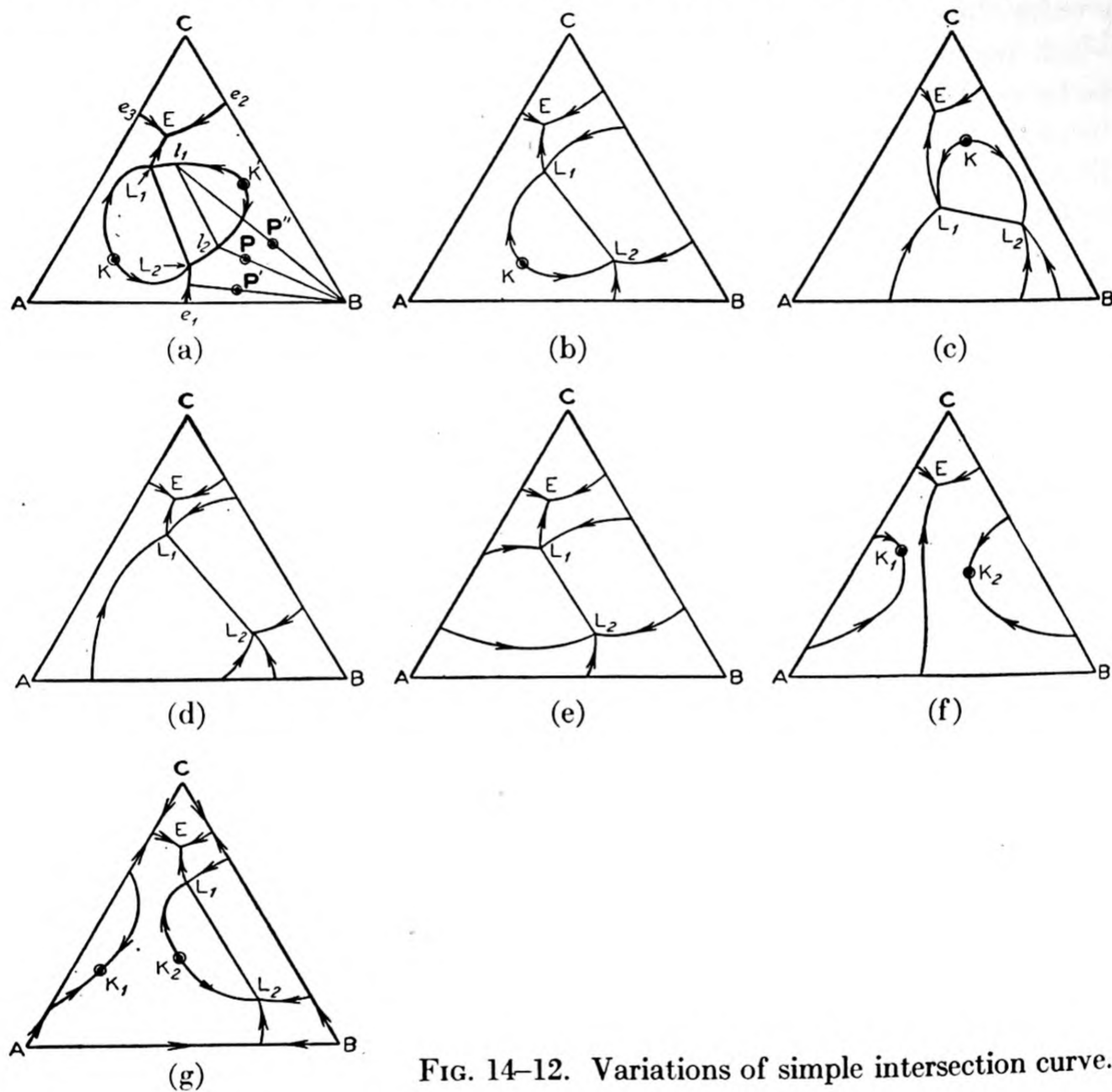


FIG. 14-12. Variations of simple intersection curve.

phases L_1L_2AB , an invariant point of type A (Chapter X). It is approached from high T by the 3-phase systems l_1l_2A from point K , l_1l_2B from point K' , and l_2AB from e_1 ; the system l_1AB leaves it with falling T , running from L_1 to the ternary eutectic E . The latter two systems are simply the two parts of the eutectic curve e_1E , interrupted by the intersection curve of the MG . The interior phase of the 4-phase invariant triangle is L_2 , the liquid l_2 being stable only above this invariant T .

When liquid P (lying in the triangle L_1L_2B) is cooled, it reaches l_2 with crystallization of B , and there produces l_1 as a third phase. With further

cooling the two liquids diverge from each other, following the intersection curve away from K' , and reach the invariant compositions L_1 and L_2 simultaneously. At this point solid A appears and the system is invariant while L_2 is consumed in the reaction $L_2 \rightarrow L_1 + A + B + \text{cals.}$ The remaining liquid then follows the curve L_1E to E, the solidification end-point. Liquid P' reaches the invariant point Q *via* curve e_1L_2 , so that liquid l_1 , with composition L_1 , first appears, in this case, in saturation with two solids. Point Q is reached only by liquids with original compositions in the

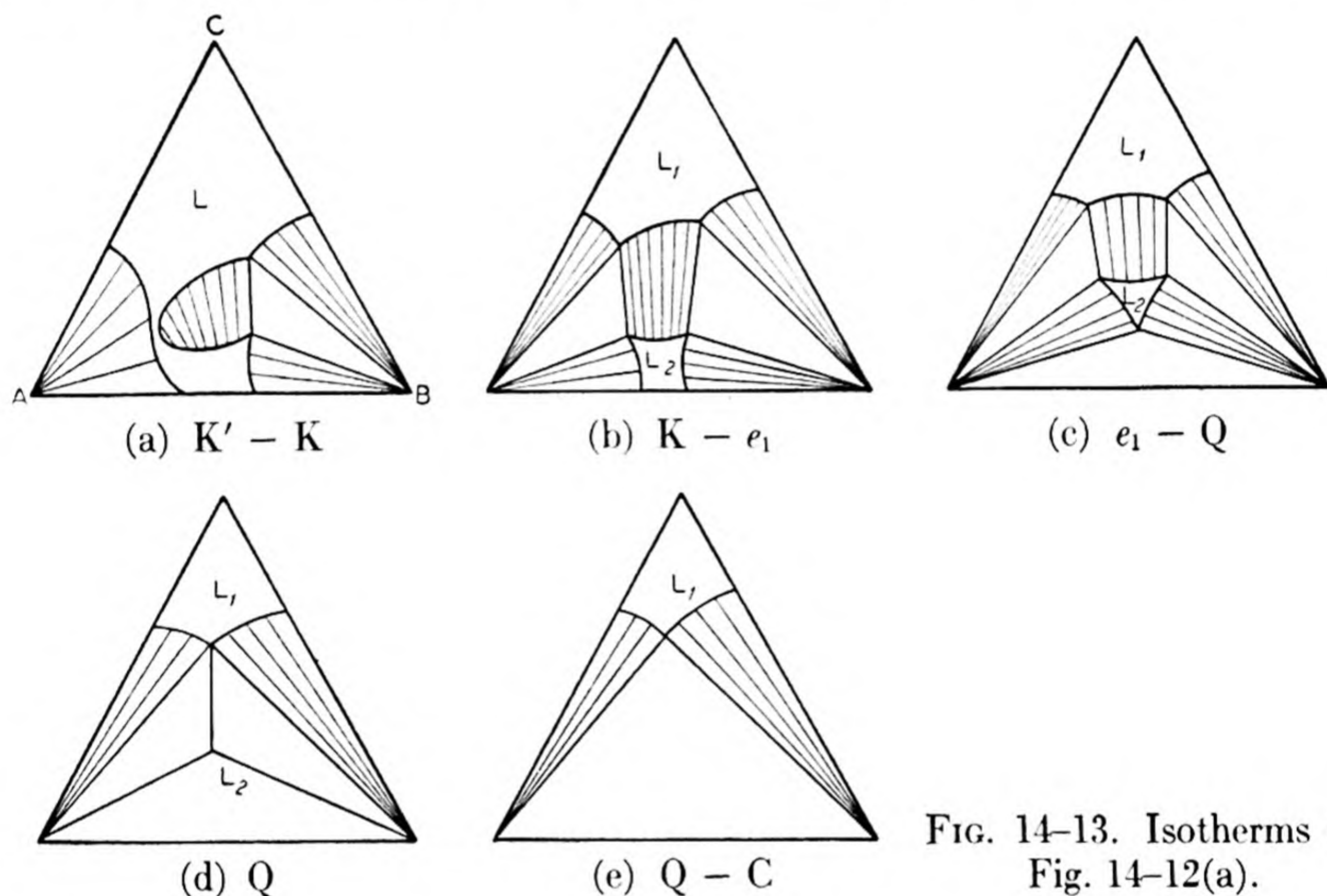


FIG. 14-13. Isotherms of Fig. 14-12(a).

triangle AL_1B . Liquid P'' , for example, which is not in this triangle, reaches the intersection curve with crystallization of B, and there produces a second liquid, on the curve L_1K' ; but the first liquid is consumed (its final composition being l_2) before solid A appears, that is, before point Q is reached, and the system l_1B then proceeds in the usual way to one of the eutectic curves L_1E or e_2E .

Cases such as Figs. 14-12(a-e) would arise when the plait point k of Fig. 14-6(b) or Fig. 14-10(b) comes to penetrate the solubility curve of a second solid phase. This is seen in the sequence of isotherms of Fig. 14-13, representing changes which would occur with falling T , with the order of temperatures for Fig. 14-12(a) assumed to be $K' > K > e_1 > Q > C$.

4. Compounds Involved

Since the intersection of the MG with crystallization surfaces does not affect the ultimate crystallization of the system, what has just been said

applies equally well if the crystallization surface or surfaces involved pertain to compounds, binary or ternary. The intersection curve may lie entirely within the field of a compound, or overlap (interrupting it into two parts) a curve of twofold saturation involving the compound.

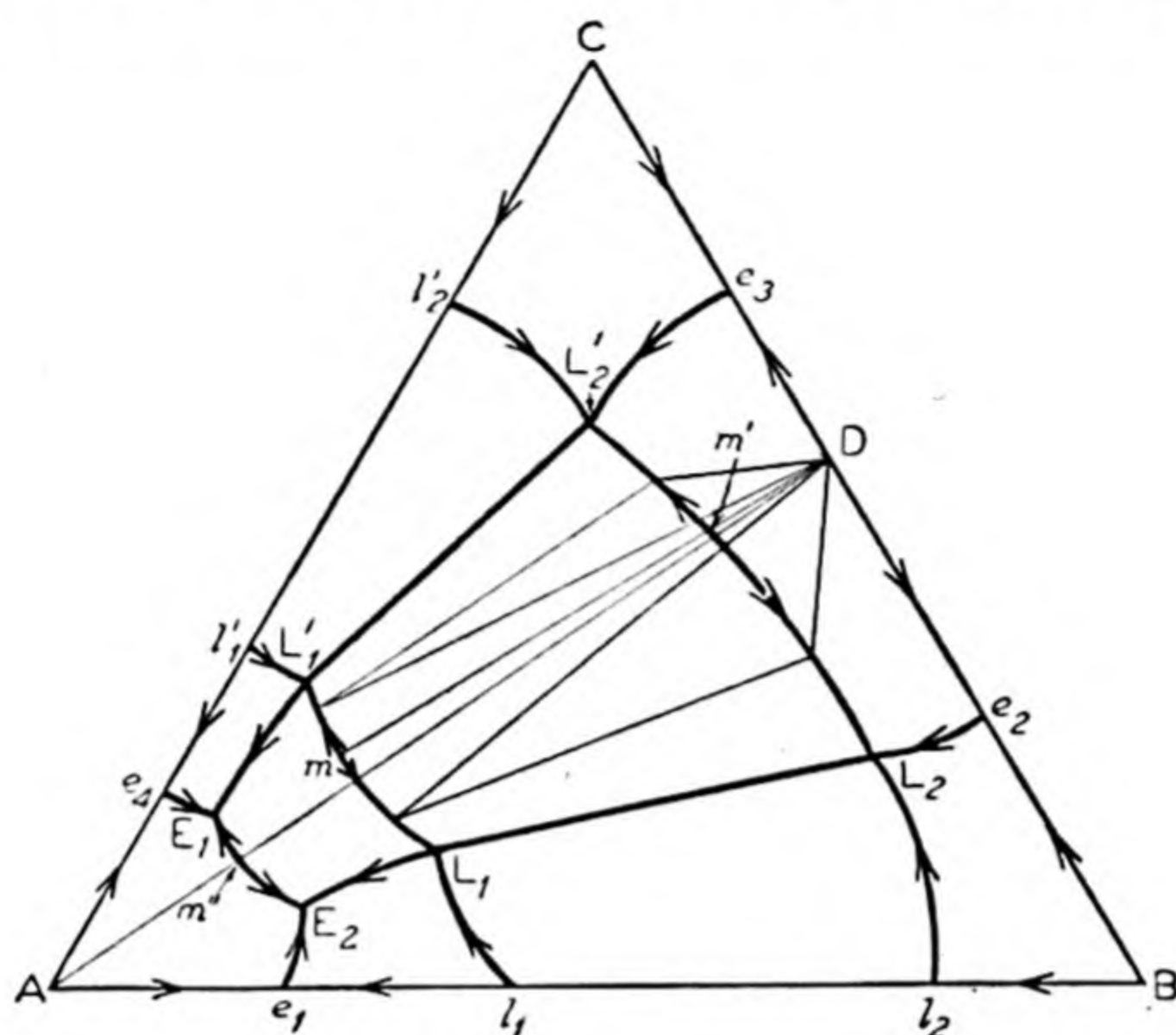


FIG. 14-14. Intersection curve on field of congruently melting binary compound.

In Fig. 14-14 a MG is shown extending, on the crystallization surfaces, from the AC side to the AB side through the field of a congruently melting binary compound D . The line $mm'D$ is a T -maximum on the intersection curve for the equilibrium l_1l_2D , similar to that in Fig. 14-7 on the field of a component. On crossing the eutectic curves e_2E_2 and e_3E_1 , this MG gives rise to two invariant points, Q for the phases BDL_1L_2 , with L_2 as interior

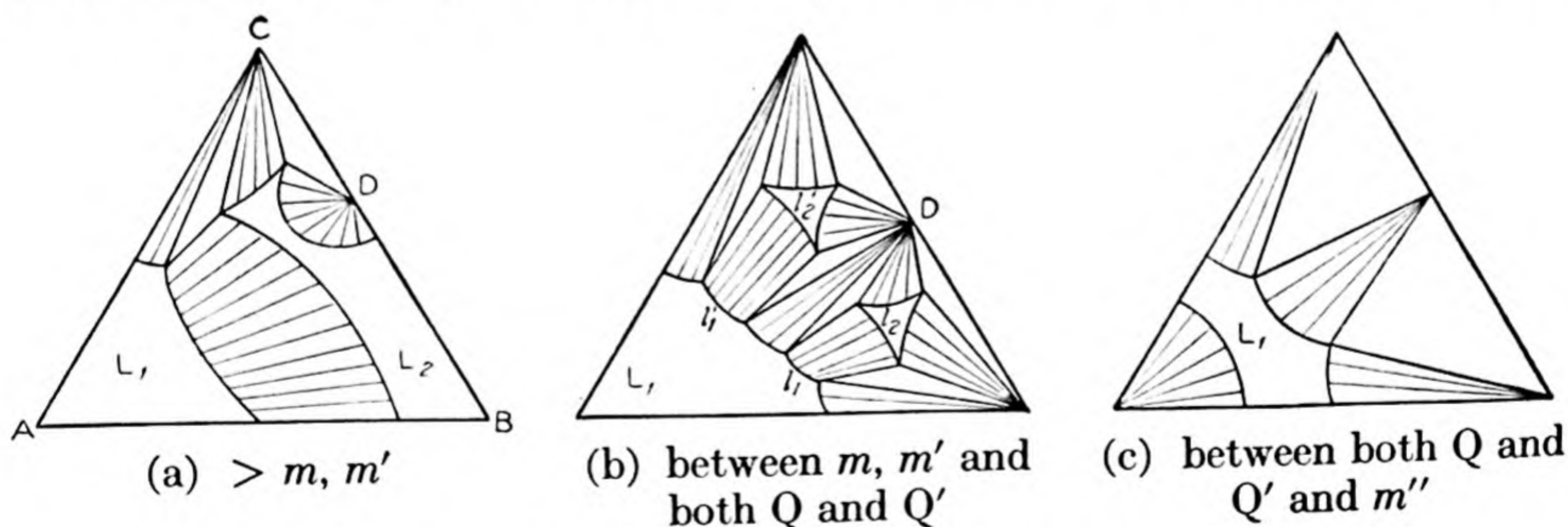


FIG. 14-15. Isotherms of Fig. 14-14.

phase, and Q' for the phases $CDL'_1L'_2$, with L'_2 as interior phase. These are similar therefore to the invariant point Q discussed under Fig. 14-12(a). Fig. 14-15 shows three isotherms for this system. At the temperature of mm' , that is, between Fig. 14-15(a) and Fig. 14-15(b), the 2-phase equilibrium for the phases l_1 and D first appears as the line $mm'D$, the contact

between the binodal curve and the solubility curve of D, of Fig. 14-15(a), occurring at a point at which the two tie-lines involved are colinear. The binodal region is then split into two parts, as shown in Fig. 14-15(b). At the invariant points Q and Q', respectively, the 2-liquid regions for $l_1 + l_2$ and $l'_1 + l'_2$ vanish to the lines L_1L_2 and $L'_1L'_2$ of Fig. 14-14, leaving, below both Q and Q', the isotherm of Fig. 14-15(c). Point m'' is the "saddle point" maximum of the curve E_1E_2 ; it marks the contact of the solubility curves of A and D of Fig. 14-15(c), as T continues to fall. One of the points E_1 or E_2 may be a ternary peritectic instead of a eutectic, if the liquid lies outside the triangle of its three solids (ACD or ADB). It is to be noted that

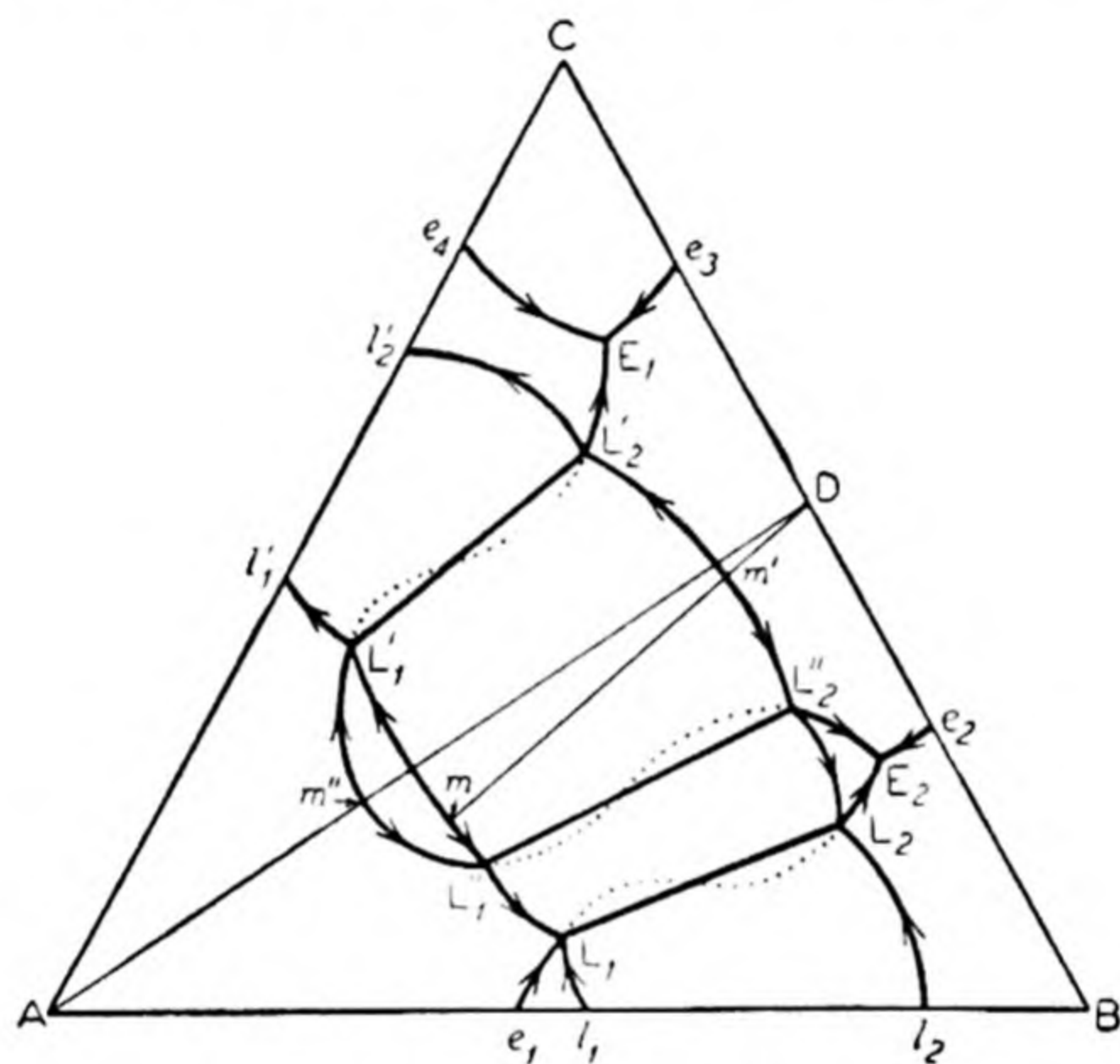


FIG. 14-16. Variation of Fig. 14-14.

the line AD is determinative, as usual, with regard to these 3-solid invariants, and that the line $mm'D$, involving one solid and two liquids, has no necessary relation to this fundamental line.

In Fig. 14-14 both the binary eutectics e_1 and e_4 are on the A side of the miscibility gap. The variations for the cases in which both these eutectics are on the BC side of the gap, or one on each side, as in the system water(A)-aniline(B)-phenol(C), shown schematically in Fig. 14-16, have been discussed by Schreinemakers.¹⁵ In this diagram the hemihydrate of phenol is disregarded (cf. Fig. 8-13). With both ternary eutectics here on the BC side of the *MG*, the 2-liquid system intersects the twofold saturation curve of liquid + A + D, running from E_1 to E_2 , twice, giving two quadruple points. One involves the phases $ADL'_1L'_2$ in the reaction $L'_1 + D \rightarrow L'_2 + A + \text{cals.}$, and the other the phases $ADL''_1L''_2$ in the reaction $L''_1 + D \rightarrow L''_2 + A + \text{cals.}$ The gap is shown furthermore as intersecting the eutectic curve e_1E_2 , of

¹⁵ F. A. H. Schreinemakers, *Z. phys. Chem.*, **30**, 460 (1899); for the system water-aniline-phenol, see also A. N. Campbell, *J. Am. Chem. Soc.*, **67**, 981 (1915).

liquid saturated with A and B, at the quadruple point AL_2BL_1 for the reaction $L_1 \rightarrow A + B + L_2 + \text{cals.}$ The points m , m' , and m'' have the same meaning as the corresponding points in Fig. 14-14.

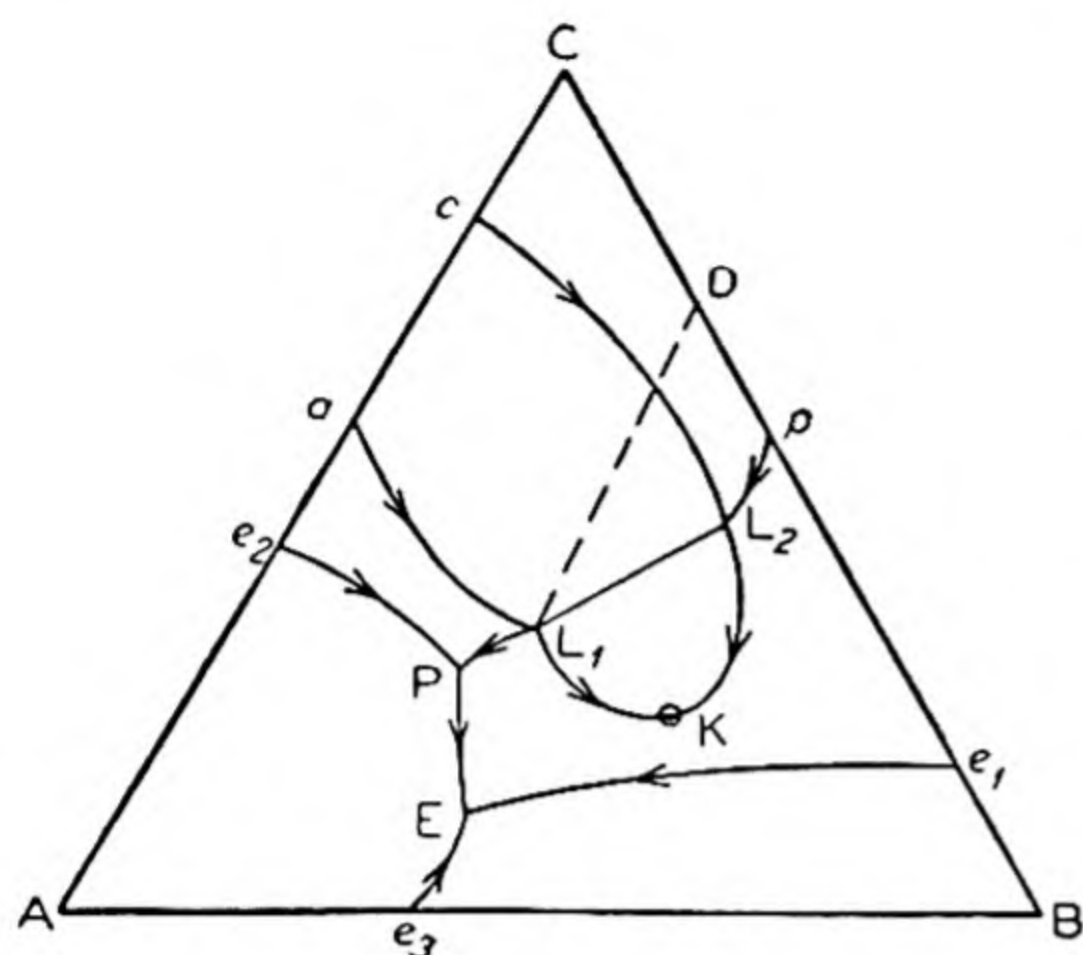


FIG. 14-17. Intersection curve and incongruently melting binary compound.

In Fig. 14-17 the intersection curve crosses the peritectic curve (pP) of the incongruently melting compound D, giving rise to an invariant point Q, of type B, involving the phases CL_1L_2D . This invariant point is reached only by liquids with original composition in the invariant quadrangle CL_1L_2D . Liquids on the left of the line CL_1 , for example, may give the equilibrium Cl_1l_2 temporarily, but will lose l_2 and reach the curves e_2P and L_1P in the usual way. Liquids on the right of

the line DL_2 will cross the transition curve pL_2 in the usual way, and may then, temporarily, split into two liquid layers while saturated with D alone, on reaching the intersection curve on the branch L_2K .

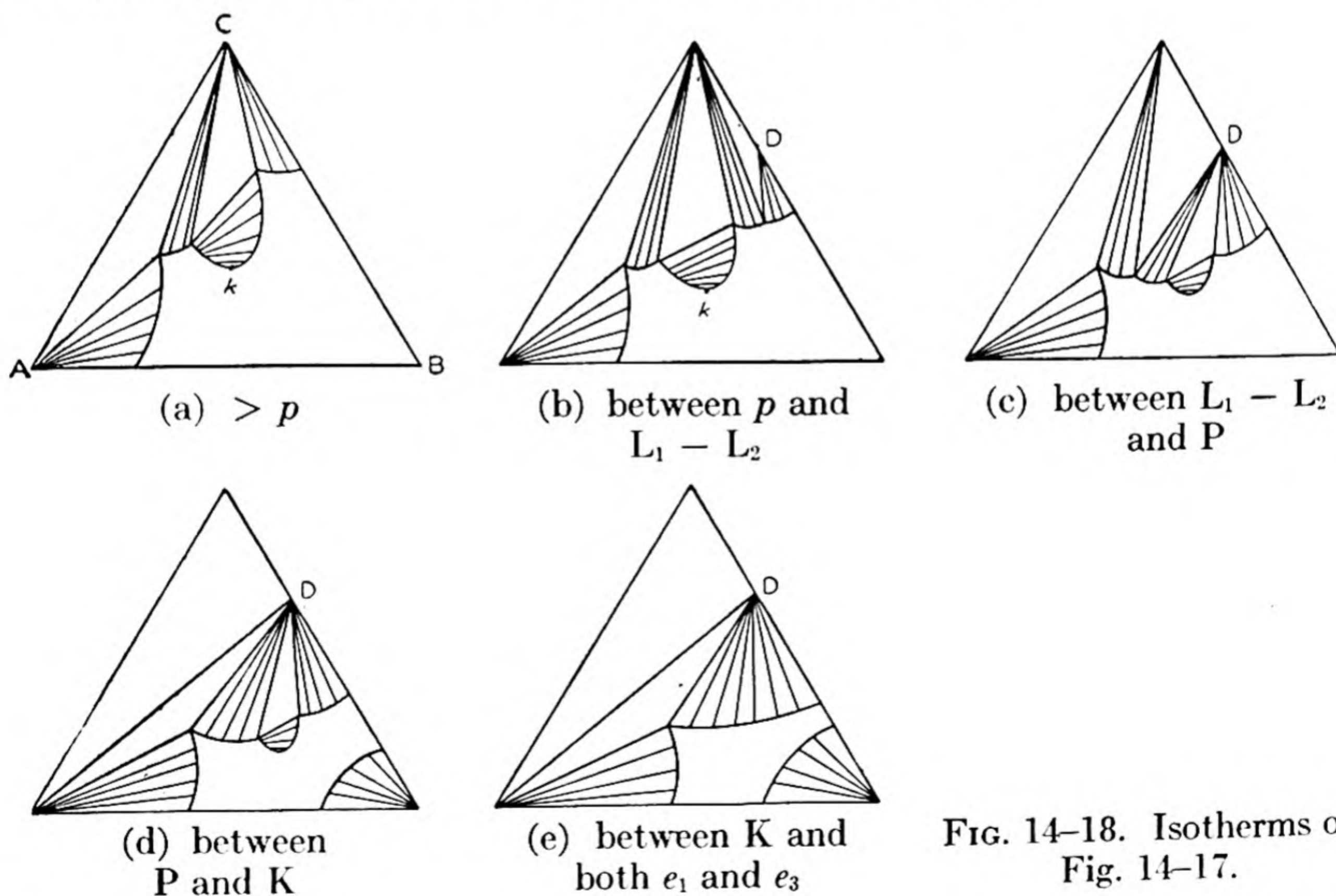


FIG. 14-18. Isotherms of Fig. 14-17.

The reaction at the diagonal invariant Q is $C + L_2 \rightarrow D + L_1 + \text{cals.}$; or, the stable diagonal changes from CL_2 above Q to DL_1 below Q. Liquids in the triangle CL_1L_2 reach Q via the curves aL_1 and cL_2 , as 2-liquid systems

saturated with solid C, and those in the triangle CDL_2 reach it *via* the curve pL_2 , as the system liquid (l_2) dissolving C and precipitating D. At the invariant point, those in the triangle CDL_1 lose the L_2 phase, and travel along the odd curve L_1P , with the reaction $C-, D+$; as explained in Chapter XII, they reach P only if the total composition lies in the triangle CDP , otherwise crossing the curve L_1P into the D field without reaching P. Liquids in the triangle DL_1L_2 lose the C phase at the invariant Q, and then proceed along the intersection curve L_1L_2K as conjugate liquids precipitating D, finally leaving this curve when one of the liquids is consumed. Some isotherms of this system are shown in Fig. 14–18.

The polytherms of Fig. 14–19 involve a binary compound of the type discussed in Chapter VIII, Section F, with a melting point submerged in a

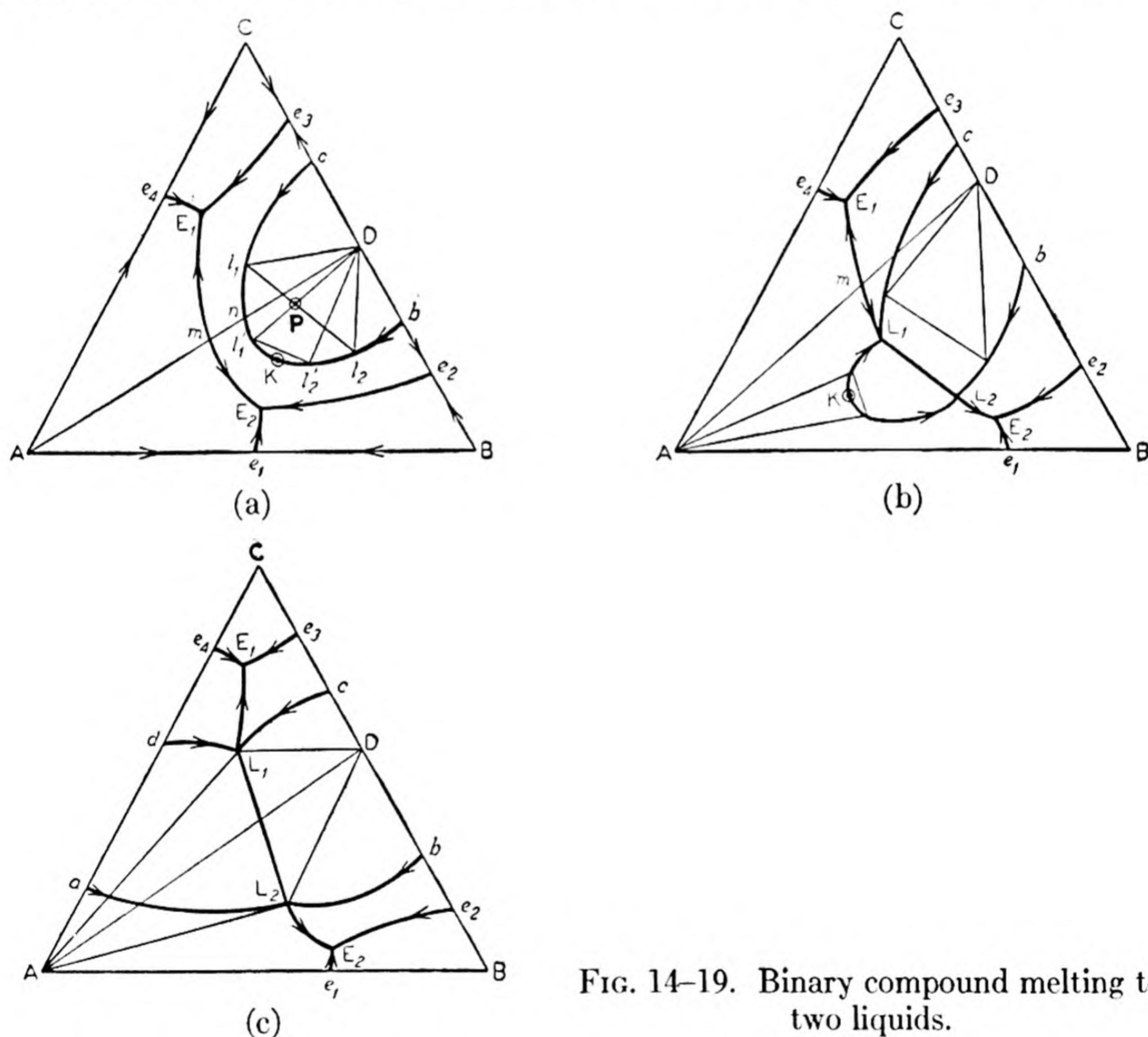


FIG. 14–19. Binary compound melting to two liquids.

MG, or decomposing into two liquids. In the simplest case, Fig. 14–19(a), the intersection curve is confined to the D field. Here the vertical section of the T/c prism through A and D would be quasi-binary if D were stable up to its melting point; but the pure compound decomposes, below its melting point, into the liquids $c(=l_1)$ and $b(=l_2)$; the section is shown in

Fig. 14-20. The horizontal n,D of this figure is one side of a 3-phase triangle (l_1l_2D), the side l_1D when it lies on the line AmD of Fig. 14-19(a), and hence with l_1 at point n . Fig. 14-21 shows an isotherm of the system of Fig. 14-19(a) between e_2 and E_2 and between e_3 and E_1 . The point l_1 of this figure moves across to the B side of the line AD , with falling T , before the temperature of the saddle point m is reached, when the solubility curve of D meets that of A on the line AD .

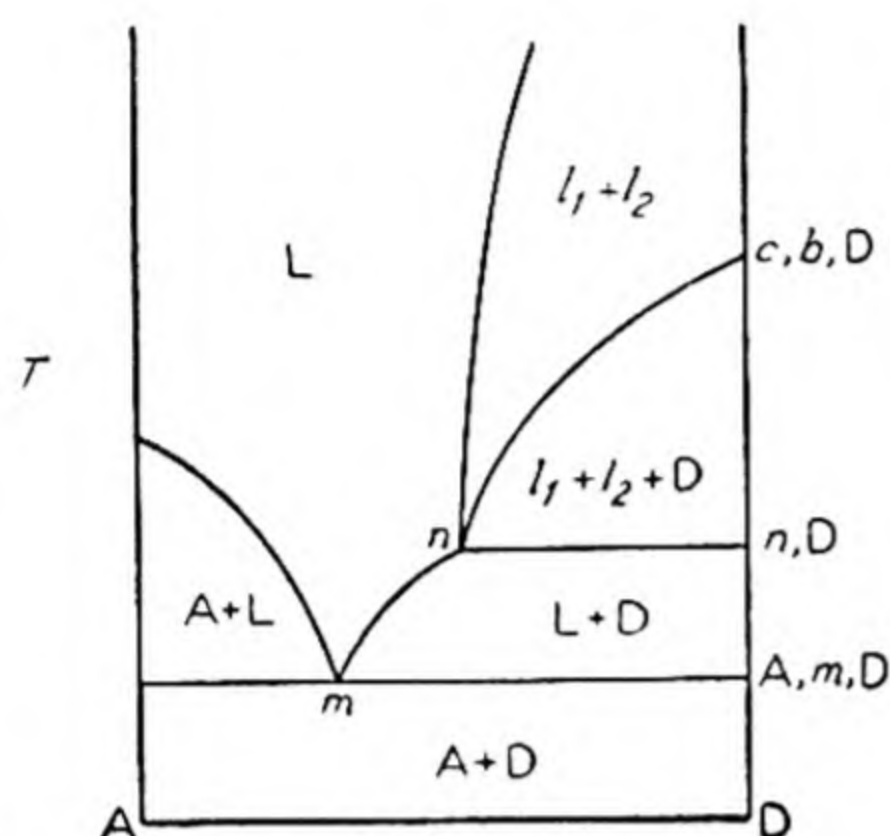


FIG. 14-20. Vertical section of Fig. 14-19(a).

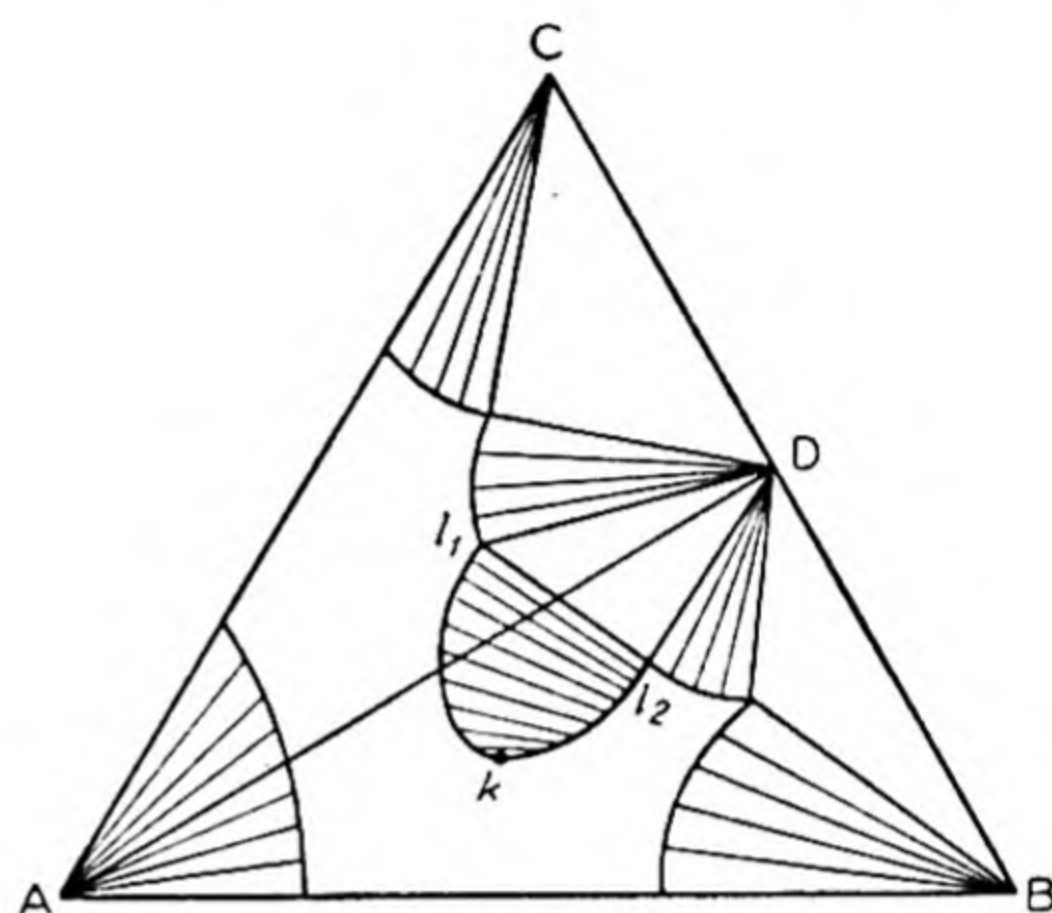


FIG. 14-21. Isotherm of Fig. 14-19(a); $T > n$.

A composition P within the intersection curve cKb consists of two liquids, l_1 and l_2 , when it begins to precipitate D . With falling T these liquids converge toward K , while precipitating D ; but when one of the lD tie-lines, in this case l_1D , meets point P , one of the two liquids, here l_2 with composition l'_2 , disappears, leaving $l'_1 + D$. The remaining liquid then moves across the D field on a straight line crystallization path away from point D , in the usual way, until it reaches one of the boundary curves leading to the eutectics. All compositions on the C side of DK leave the intersection curve as $l_1 + D$, and those on the B side as $l_2 + D$. But as usual, all compositions in the triangle ACD complete their solidification at E_1 and those in ABD at E_2 . One of these points may be a ternary peritectic, but the 2-liquid phenomena would remain as already described, purely temporary phenomena in the course of solidification.

The intersection curve of the compound D may overlap any one of the ternary boundaries of the D field, with K in one of the adjacent fields, as in Fig. 14-19(b), and it may extend to one of the other binary sides, as in Fig. 14-19(c). In Fig. 14-19(b) the intersection curve interrupts the curve mE_2 of Fig. 14-19(a), to give the invariant point Q , type $A, L_1 \rightarrow A + D + L_2 + \text{cals.}$, terminal for L_1 with falling T and reached, on cooling, by all compositions in the triangle ADL_2 on their way to E_2 . The critical solution point K is a maximum on the intersection curve L_1KL_2 , since it lies on the crystallization surface of A , rising toward A . The conjugate liquids in this

section are saturated with A while those in the portion of the intersection curve in the D field are, of course, saturated with D. Fig. 14-22 is an isotherm of Fig. 14-19(b) between the saddle point temperature m and L_1 (or the invariant point Q), below e_2 and above e_1 , and just above E_1 . In Fig. 14-19(c) the intersection curve has engulfed the saddle point m , and

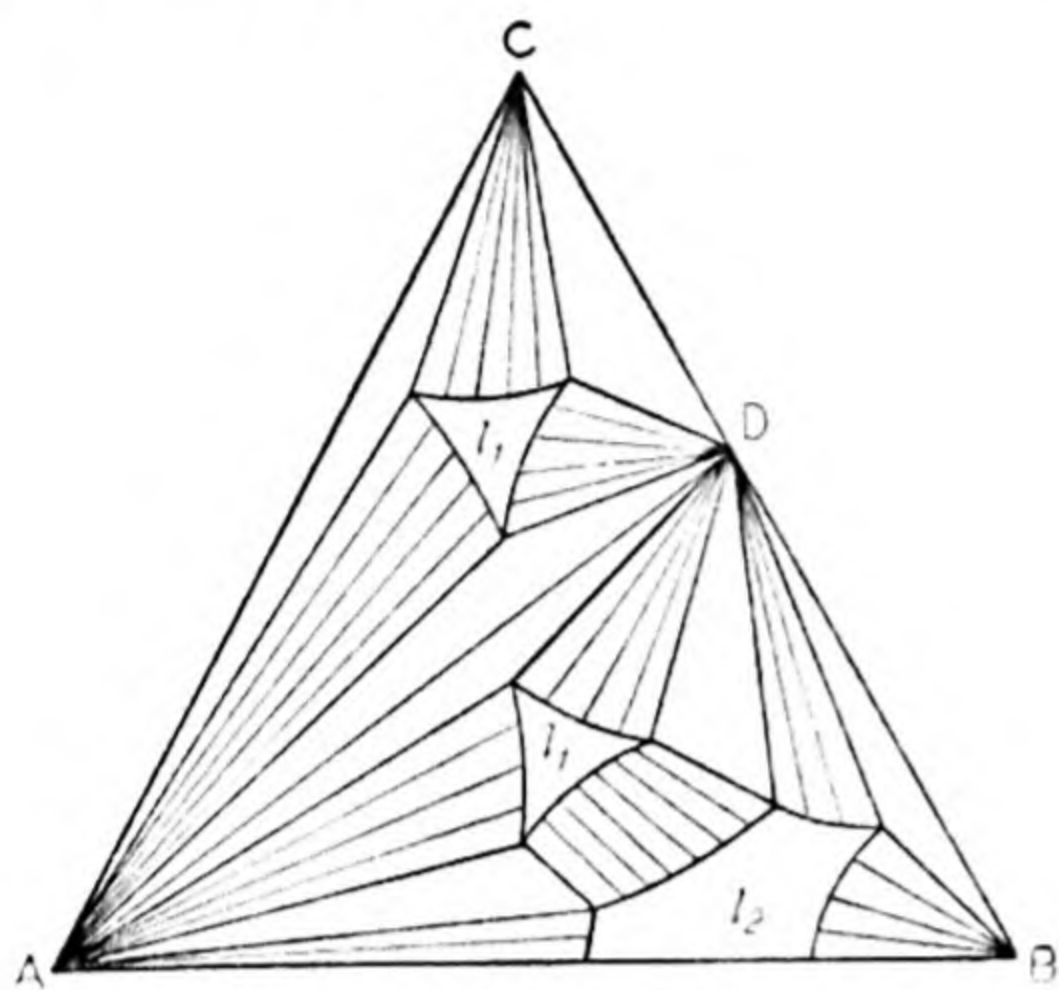


FIG. 14-22. Isotherm of Fig. 14-19(b).

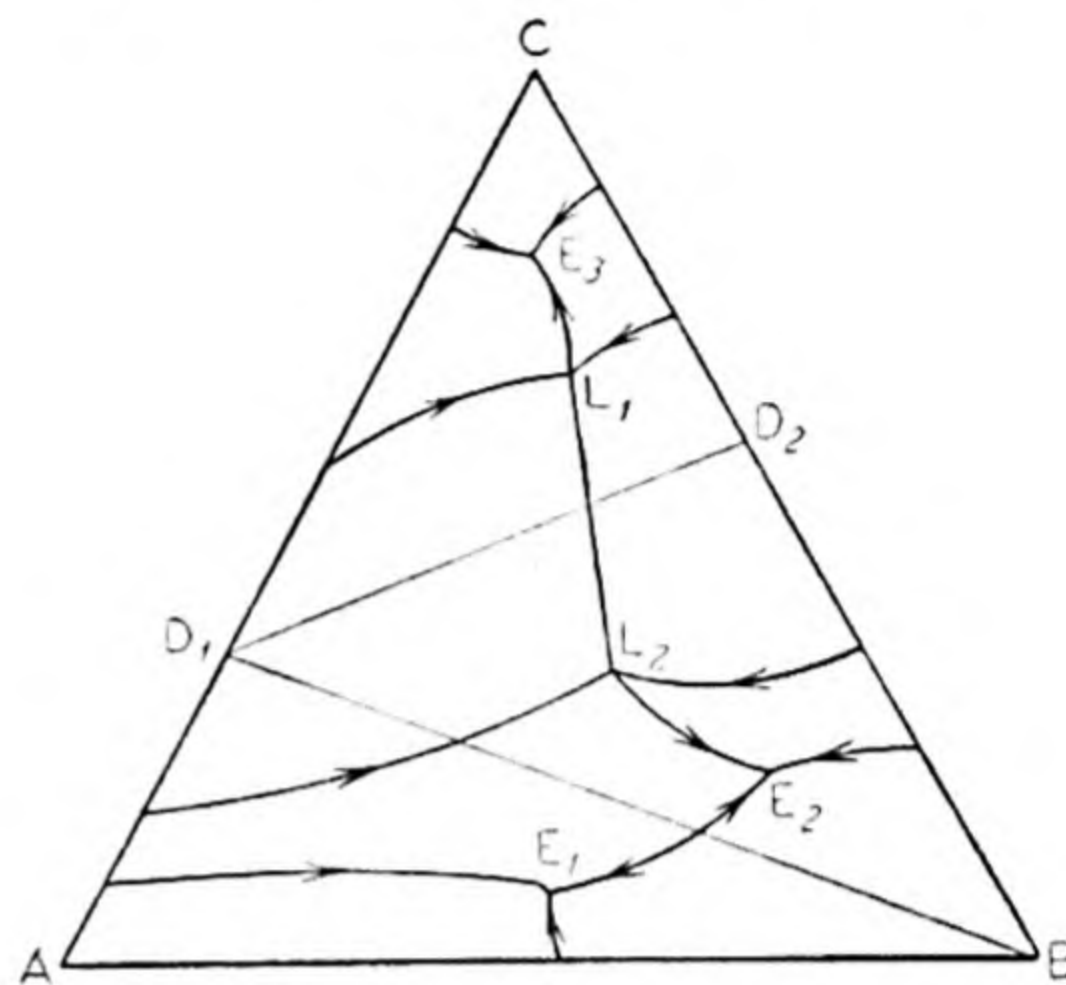


FIG. 14-23. Two binary compounds melting to two liquids.

in addition it reaches the binary side AC in the A field. Now the invariant Q, involving the same four phases as that of Fig. 14-19(b), is a diagonal invariant, type B, with the reaction $L_1 + L_2 \rightarrow A + D + \text{cals.}$ It is reached, on cooling, by compositions in the quadrangle AL_1DL_2 , and it is a maximum temperature point on the interrupted curve between E_1 and E_2 . It is reached by the 3-phase systems Al_1l_2 from the AC side and l_1Dl_2 from the D side. Liquids originally in the triangle AL_1D , however, must end at E_1 , so that these lose the L_2 phase at Q, to travel, as the system l_1AD , to E_1 on the curve L_1E_1 ; for those in the triangle AL_2D , L_1 is consumed at Q, since the solidification must end at E_2 .

In Fig. 14-23, each of the two binary compounds D_1 and D_2 decomposes to two liquids, and the MG , running from one binary side to the other, intersects the twofold saturation curve joining the ternary eutectics E_1 and E_2 . The reaction at the diagonal invariant (Q_B) equilibrium of this intersection is $L_1 + L_2 \rightarrow D_1 + D_2 + \text{cals.}$

In Fig. 14-24 the MG under discussion overlaps the field of a ternary compound D' , giving a similar diagonal invariant, Q_B , with the reaction $L_1 + L_2 \rightarrow D + D' + \text{cals.}$ The conjugate liquids on the D side of the invariant diagonal L_1L_2 are saturated with D, while those on the D' side are saturated with D' . This invariant (like that of Fig. 14-23) is therefore entirely similar to that of Fig. 14-19(c), leading, from L_1 , to the ternary eutectic E_3 for the solids C, D, and D' , and, from L_2 , to the ternary peritectic P for the reaction $L(P) + D \rightarrow D' + B + \text{cals.}$ Point P is the incon-

gruent solidification end-point for the triangle BDD'. If the intersection curve in the D' field did not extend so far as to include the point D', the relations would be altogether similar, in short, to those in Fig. 14-19(b), with D' in place of A. But with D' engulfed by the intersection curve, then solid D', heated at the pressure of the figure, decomposes, before reaching an

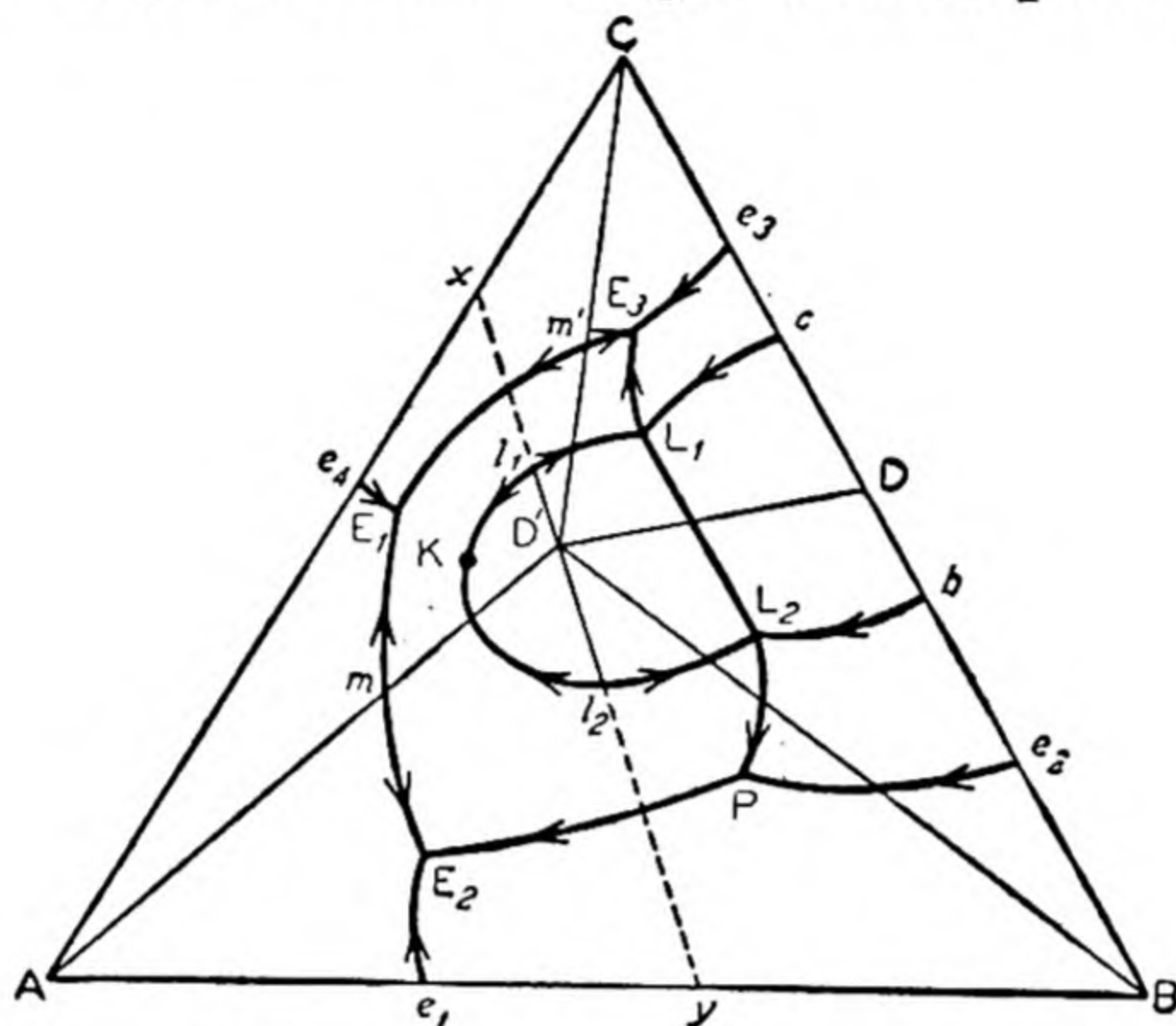


FIG. 14-24. Ternary compound melting to two liquids.

ordinary melting point, into two liquids, l_1 and l_2 , represented by the ends of a tie-line spanning the intersection curve and passing through D'; the phenomenon is analogous to the decomposition of D, in the binary system C-B, to give the liquids c and b on the side CB. The tie-line $l_1D'l_2$ is a point of maximum temperature on the intersection curve in the D' field, the 3-phase equilibrium of D' + two liquids falling in T , on one side to the critical point K and on the other to the invariant point Q_B on the tie-line L_1L_2 . The direction of the decomposition point tie-line $l_1D'l_2$ cannot be predicted merely from the compositions of the solid phases and the positions of the invariants. For the system of condensed phases, in absence of vapor, this decomposition point is an invariant point at arbitrary pressure. When the pure compound D' is heated, at such arbitrary constant pressure, the temperature of the system undergoing the reaction $D' \rightleftharpoons l_1 + l_2 - \text{cals.}$ remains constant until all the solid has decomposed. With three components in three phases at constant pressure, F here equals 0 because of the composition restriction that the compositions of the two liquids are colinear with D' (cf. Fig. 12-68(a)). The position of the line xy , corresponding to this colinear equilibrium of D and two liquids, presumably depends on the pressure. The two liquids are therefore produced in an invariant reaction at constant T , with fixed compositions and in a fixed ratio, such that the total composition equals D'. With vapor present, the 4-phase equilibrium is a singular point, type m , with $F = 0$ by restriction.

Two-liquid systems with compositions in the intersection curve L_1KL_2 precipitate D' when cooled to the temperature of this 3-phase curve. If the composition lies on the line l_1l_2 the precipitation of D' is an invariant reaction, proceeding to completion, invariantly, if the total composition is that of D' itself. If it is on the line l_1l_2 , but not at point D' , the reaction $l_1 + l_2 \rightarrow D' + \text{cals.}$ is invariant, until one of the liquids is consumed. For compositions between l_1 and D' , l_2 is consumed, and the remaining system of $l_1 + D'$ proceeds on the line xy to the curve E_1m' , where C appears, and finally to E_1 to leave $A + C + D'$. For compositions between D' and l_2 , l_1 is consumed, and then the curve PE_2 is reached on the line xy , and finally E_2 to leave $A + B + D'$. The points m and m' , it may be noted, are both saddle points on their respective curves.

B. Three Liquid Phases

If the isobarically univariant equilibrium involving three liquid phases l_1 , l_2 , and l_3 , intersects the crystallization surface of a solid, an invariant point involving three liquids and a solid is the result. Again the relations are essentially the same whether the solid is a component or a compound, provided the 3-phase triangle $l_1l_2l_3$ does not include the composition of a (ternary) compound.

1. Illustrating the first possibility with the field of a component, we have the polythermal projection of Fig. 14-25. The isothermal triangle $L_1L_2L_3$

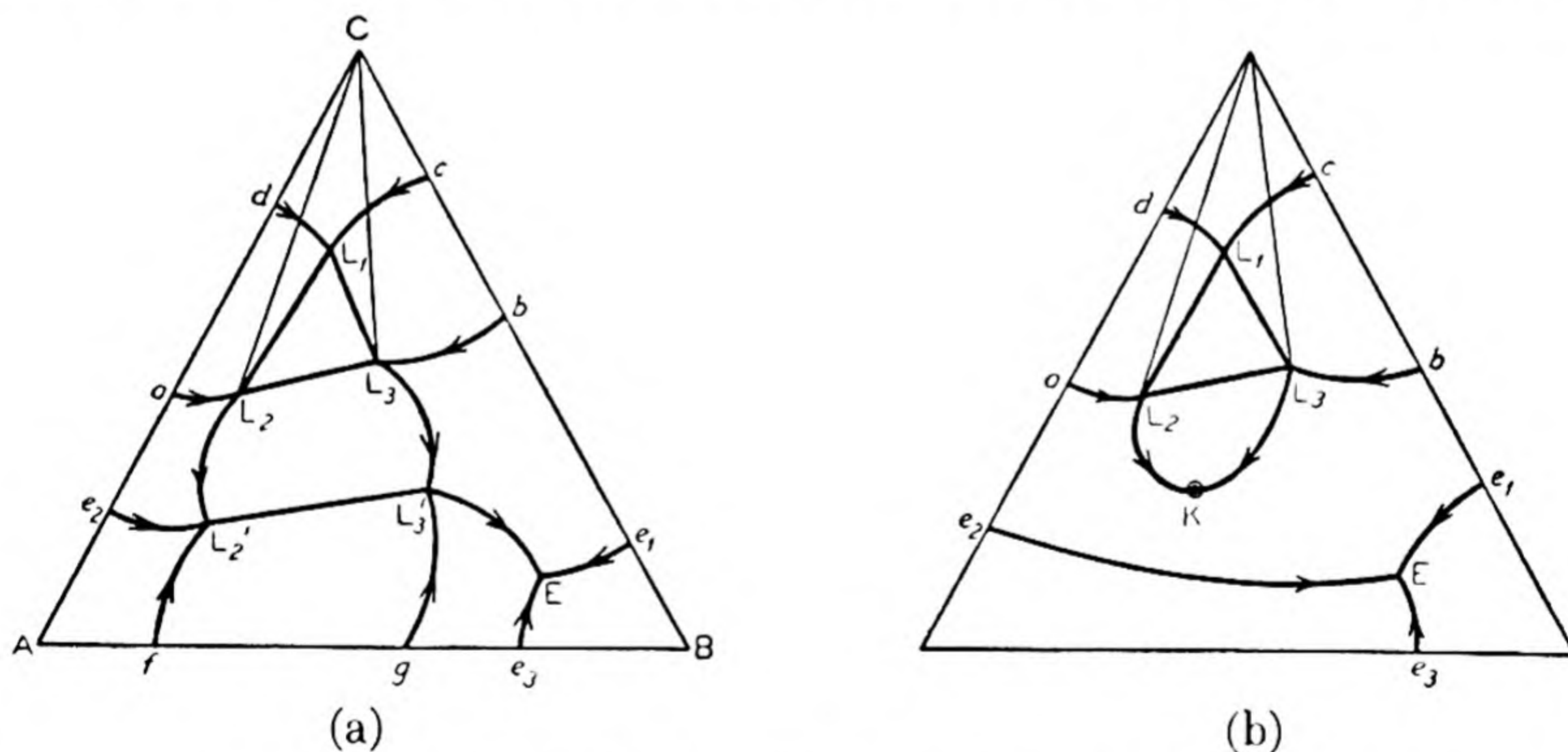


FIG. 14-25. Invariant equilibrium of solid + 3 liquids.

represents three liquids simultaneously saturated with solid C, so that the three liquids are part of the 4-phase invariant equilibrium Q for the phases $CL_1L_2L_3$. The crystallization surface of C is intersected by three binodal curves, which meet at this invariant point, and which may or may not reach the boundaries of the C field. In both figures, 14-25(a) and (b), two

of the binodal curves are shown reaching binary sides, the AC side at ad and the BC side at bc . Either of these could also end at critical solution points. The third binodal curve is thus shown ending at a critical solution point in the C field, in Fig. 14-25(b); but in Fig. 14-25(a) it not only crosses the eutectic curve e_2E into the A field but reaches the binary side AB at fg .

The invariant equilibrium Q is reached, on cooling, only by compositions falling in the figure, triangular or quadrangular, defined by its four phases C, L_1 , L_2 , and L_3 . If the two 3-phase equilibria CL_1L_2 and CL_1L_3 both approach Q from higher temperature (together with the $L_1L_2L_3$ equilibrium), then the invariant is of type A, terminal with respect to the interior phase L_1 , as is assumed in Fig. 14-25. If one of the two equilibria mentioned approaches Q from lower T , the invariant will be of the diagonal type (type B), with L_1 outside the triangle CL_2L_3 .

For the case assumed in Fig. 14-25, the invariant Q is reached only by compositions in the triangle CL_2L_3 . At Q the phase L_1 disappears, leaving the equilibrium CL_2L_3 as T falls below the invariant. If the intersection curve of this equilibrium is closed, as in Fig. 14-25(b), only single-liquid systems reach the curves of twofold saturation, e_2Ee_1 . If it intersects one of these curves, as in Fig. 14-25(a), there will be a second invariant, Q' , for the phases $ACL'_2L'_3$, which interrupts the eutectic curve e_2E into two parts, $e_2L'_2$ and L'_3E . If the only 3-phase equilibrium leaving this invariant point with falling T is the curve L'_3E (for liquid + C + A), the invariant Q' is of type A, terminal with respect to L'_2 , the interior phase of the triangle ACL'_3 , as assumed in Fig. 14-25(a). This type of invariant, reached by compositions in the triangle ACL'_3 , has already been discussed in connection with Fig. 14-12(a).

A system of three liquid layers, then, of such composition as to fall in the triangle $L_1L_2L_3$ of Fig. 14-25(a) when the temperature is lowered to Q, undergoes no phase changes, except for adjustment of the compositions and proportions of the three liquids, until cooled to Q, when, at constant T , solid C appears while L_1 is consumed in the reaction $L_1 \rightarrow C + L_2 + L_3 + \text{cals.}$ When L_1 has disappeared, the remaining liquids, still precipitating C, proceed as conjugate liquids along the curves $L_2L'_2$ and $L_3L'_3$ toward the second invariant Q' . This invariant is reached only by compositions in the triangle ACL'_3 . At Q' the reaction $L'_2 \rightarrow A + C + L'_3 + \text{cals.}$ proceeds until all of L'_2 is consumed, whereupon the single liquid remaining, precipitating A and C, travels on the curve L'_3E to the eutectic. If, however, for example, the point L_3 does not lie in the triangle ACL'_3 , it is possible for some compositions to pass through the first and not the second invariant point, before reaching the eutectic. Depending, therefore, upon the relations of the two invariant triangles (Q and Q') and upon the curvature of the intersection

curves between the invariant lines L_2L_3 and $L'_2L'_3$, a great variety of sequences of phenomena during cooling becomes possible.

Some schematic isotherms for Fig. 14-25(a) are shown in Fig. 14-26, in which the order of invariant temperatures, from the highest to the lowest, is assumed to be the following: C; Cda; Ccb; A; Q; Afg; B; e_2 ; Q'; e_1 ; e_3 ; E.

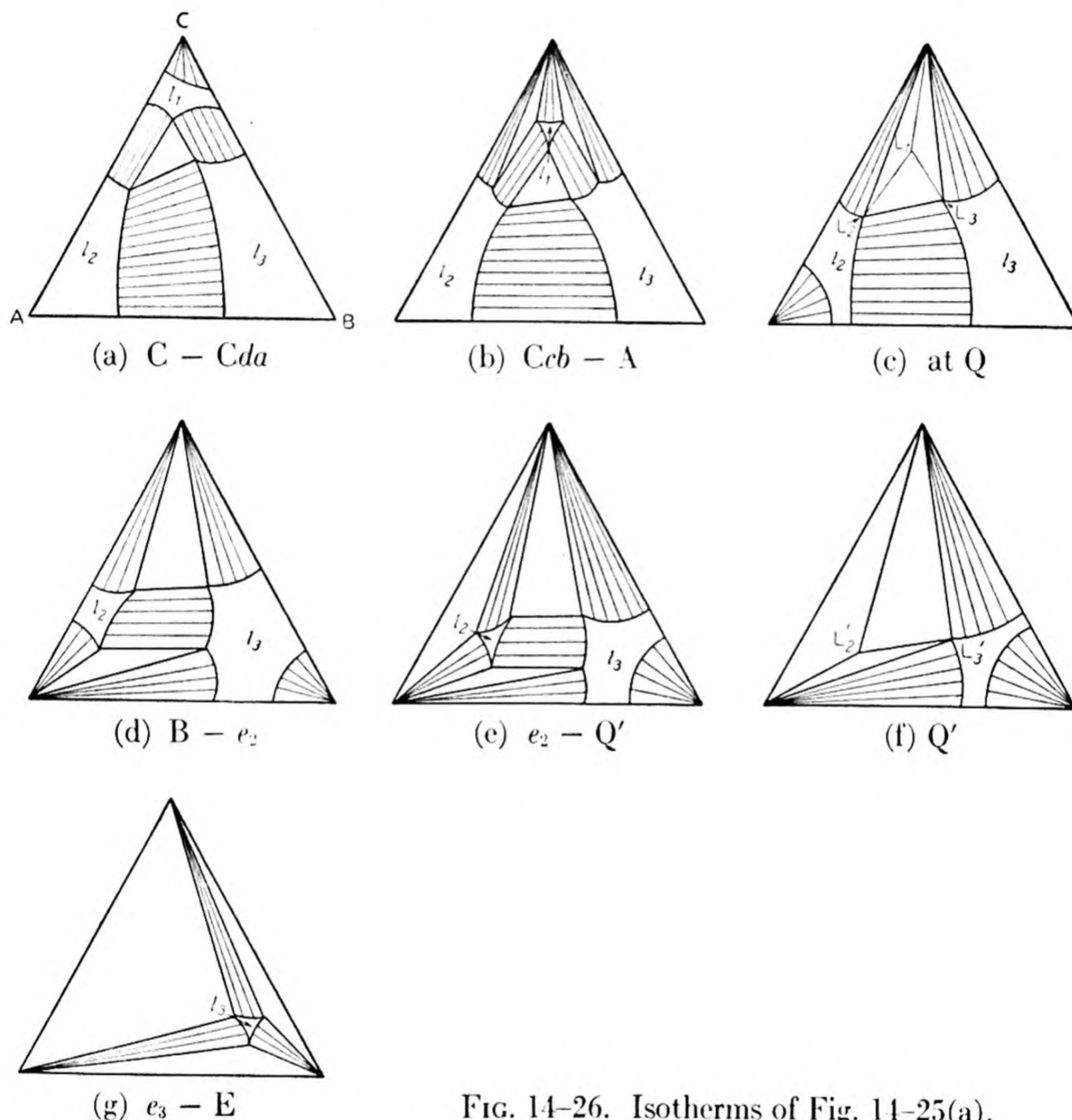


FIG. 14-26. Isotherms of Fig. 14-25(a).

2. If the 3-liquid system intersects the crystallization surface of a ternary compound in such a way as to include the composition of the compound, the situation is somewhat similar to that of Fig. 14-24. There the ternary compound decomposes to two liquids on heating, and in the present case to three. The decomposition point in the present case, however, is invariant directly as the result of the number of phases. Without pressure restriction, and with vapor present, $F = 3 - 5 + 2 = 0$. The polythermal projection of the pertinent relations is shown in Fig. 14-27. The compound is the

interior phase of the invariant 4-phase triangle $L_1L_2L_3$. If the pure compound is heated at constant pressure, it decomposes at this temperature, invariantly, to the liquids $L_1 + L_2 + L_3$, with fixed compositions and with fixed relative proportions since the total composition is that of D itself. On the other hand, if the 3-liquid system is cooled, it precipitates D at constant T . But unless the total composition is exactly D , solidification is not complete at the invariant T . One of the liquids disappears in the reaction $L_1 + L_2 + L_3 \rightarrow D + \text{cals.}$ to leave a saturated 2-liquid system. Thus if

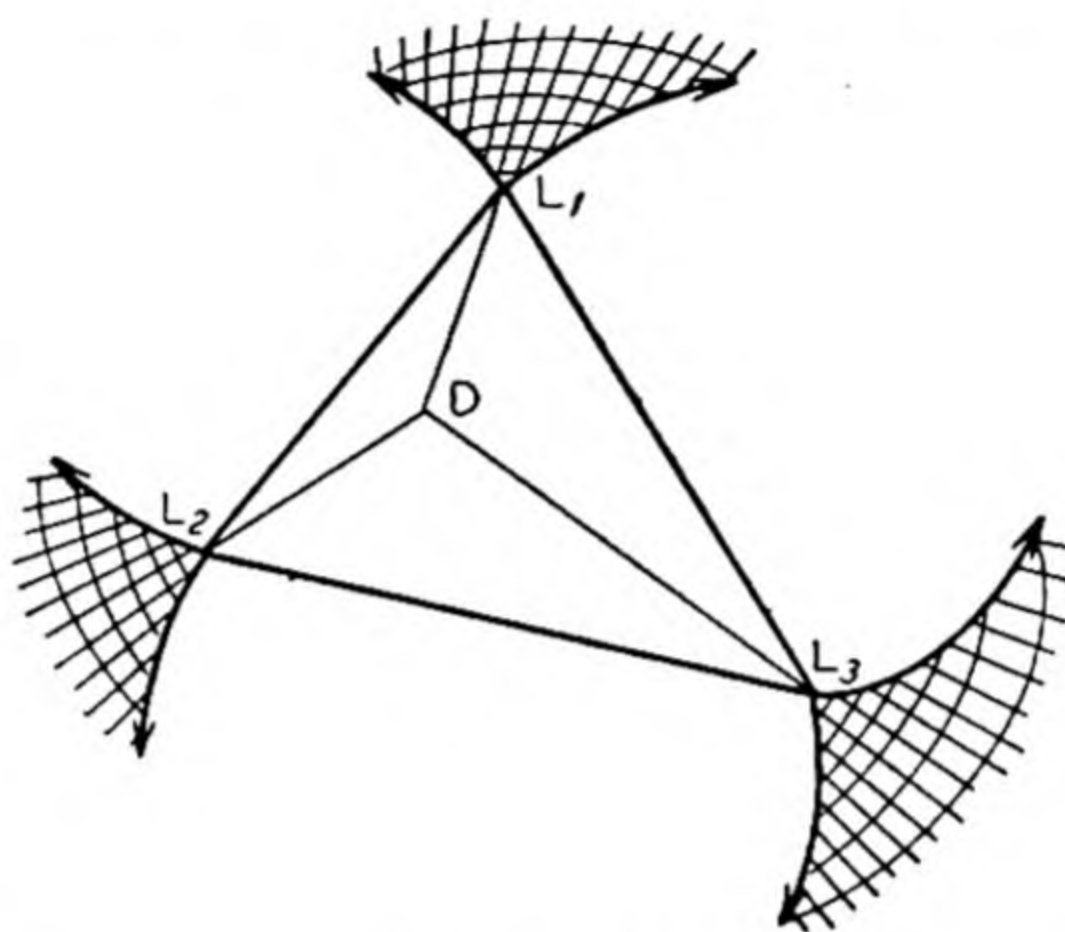


FIG. 14-27. Ternary compound melting to three liquids.

the composition is in the triangle DL_2L_3 , L_1 is consumed at constant T , leaving $D + L_2 + L_3$, one of the three such equilibria proceeding from the invariant point with falling T . The termination of any of these 3-phase equilibria (intersection curves in each case of a MG with the D field) will, as usual, be either a critical solution point or a 4-phase invariant point on a curve of twofold saturation at a boundary of the D field. Parts of the D field are shown in Fig. 14-27, with temperature contours and crystallization paths. The crystallization paths are straight lines radiating from D , and the temperature contours are concentric at D . The invariant point of Fig. 14-27, therefore, is the maximum temperature of the D field in the T/c prism.

Chapter XV Reciprocal Ternary Systems

A. Composition Units

If four substances are stoichiometrically related in the double decomposition $AB + CD \rightleftharpoons AD + CB$, the system consisting of these four substances is ternary because all possible compositions may be expressed in terms of any three of them (as explained in Chapters I and X). If the three substances taken as components are chosen arbitrarily, the composition may involve negative terms, but it is always possible to express any given composition in terms of positive percentages of three substances suitably chosen.

Since the system is ternary, only two of the three composition terms (percentages) have to be determined or represented in order to define the total composition, since the sum of the three percentages always equals one hundred. This means that the chemical analysis of a ternary mixture requires only two determinations. It is sufficient to determine the quantities (either in grams or in equivalents) of any two of the radicals A, B, C, and D per 100 grams of sample to establish the composition of the sample, since the sum of the "positive" equivalents, such as A and C, must equal the sum of the "negative" equivalents B and D. When the number of equivalents of each of the four radicals per 100 grams of sample is thus determined, the result may be expressed in terms of any three of the four formulas or substances, and it is only for convenience that particular care may be taken to choose these three substances so that the percentage of each will be positive.

The final result for a given composition may therefore be tabulated in any one of the three sets of units illustrated in Table 15-1: (a) weight percentage, or number of grams of each of three substances, or the components, per 100 grams of total; (b) number of equivalents of each of three substances, again the components, per 100 equivalents of total, or the "equivalent percentages"; (c) the equivalent percentage of the radical C in the sum of A and C, and the equivalent percentage of D in B + D. In method (c) we do not have to specify three particular substances as the components, but merely speak of the reciprocal ternary system. It is clear in any case that we need plot only two composition variables on a plane figure, for in

methods (a) and (b) the percentage of the third substance is fixed as the difference from 100.

TABLE 15-1. TABULATION OF COMPOSITION DATA
Analysis: 21.21 wt. % A, 37.88 wt. % D
Equivalent weights: A, 20; B, 30; C, 40; D, 50

METHOD (a) — *Weight percentages of three compounds*

AB	CD	AD	CB
37.9	40.9	21.2	...
53.0	68.2	...	— 21.2
15.2	...	53.0	31.8
...	— 27.2	74.2	53.0

METHOD (b) — *Equivalent percentages of three compounds*

AB	CD	AD	CB
50	30	20	...
70	50	...	— 20
20	...	50	30
...	— 20	70	50

METHOD (c) — *Radical proportions: Equivalents of radicals per 100 equivalents of compounds*

A	C	B	D
70	30	50	50

$$N_+ = C/(A + C) = 0.3; N_- = D/(B + D) = 0.5$$

B. Plotting

We shall start by considering the plotting of compositions listed according to method (b), although the actual diagram obtained turns out to be identical with that for method (c). (Representation in units other than reciprocal equivalents would not be useful, and will not be considered.) The simplest plane figure for the purpose is the square (Fig. 15-1), with each corner representing one of the four substances and with the side taken as unity, or 100% (always in equivalents). The diagonal AB-CD is included because we shall take AB, CD and AD as the components. In this case the percentages of AB and CD will be positive for all possible compositions, but the percentage of AD will be positive in triangle I and negative in triangle II. Since the side is the unit, the percentage of AB at a point (**P** or **P'**) is measured vertically from the top to the point, the percentage of CD horizontally from the left side to the point, and the percentage of AD from the diagonal to the point, horizontally or vertically. It will be seen that the point **P'** may be expressed in three positive terms if the components are taken either as AB, CD, and CB, or as AD, CB, and CD.

Each corner then represents a pure substance, the sides represent binary compositions of substances with a common radical, and the interior includes all ternary compositions. Compositions made from a reciprocal pair fall on a diagonal.

As in the case of the composition triangle for additive ternary systems, this composition quadrangle need not have any particular shape. It may be a parallelogram, either with equal sides or with two side lengths, as in Fig. 15-2, the percentages being measured parallel to the sides; if the sides are

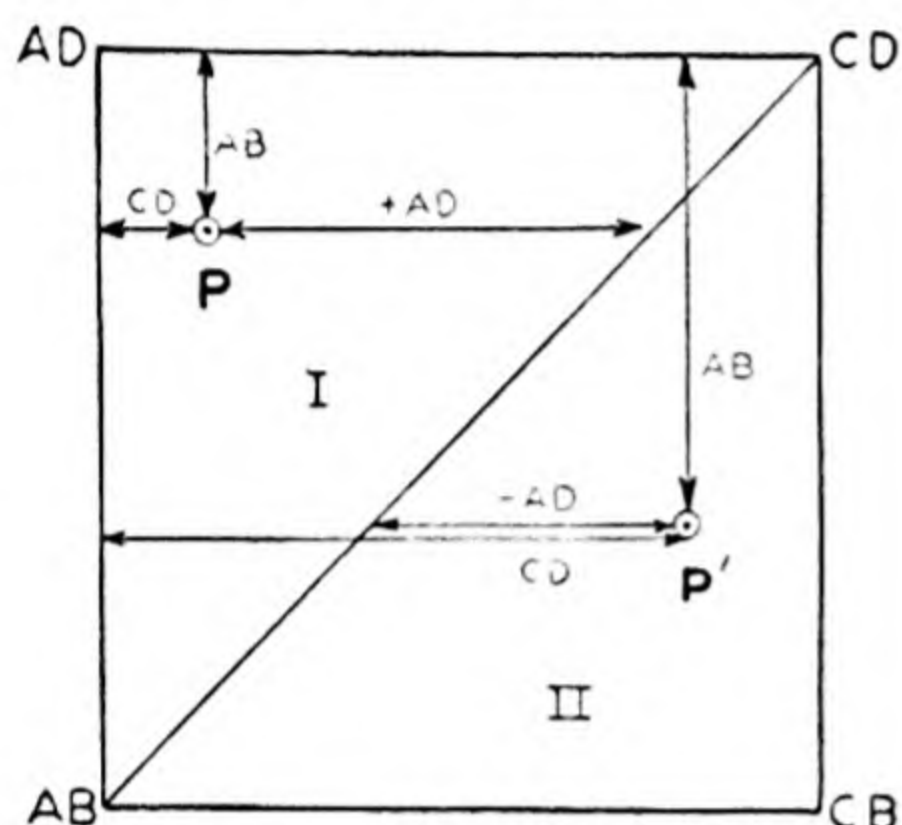


FIG. 15-1. Square figure in terms of three compounds.

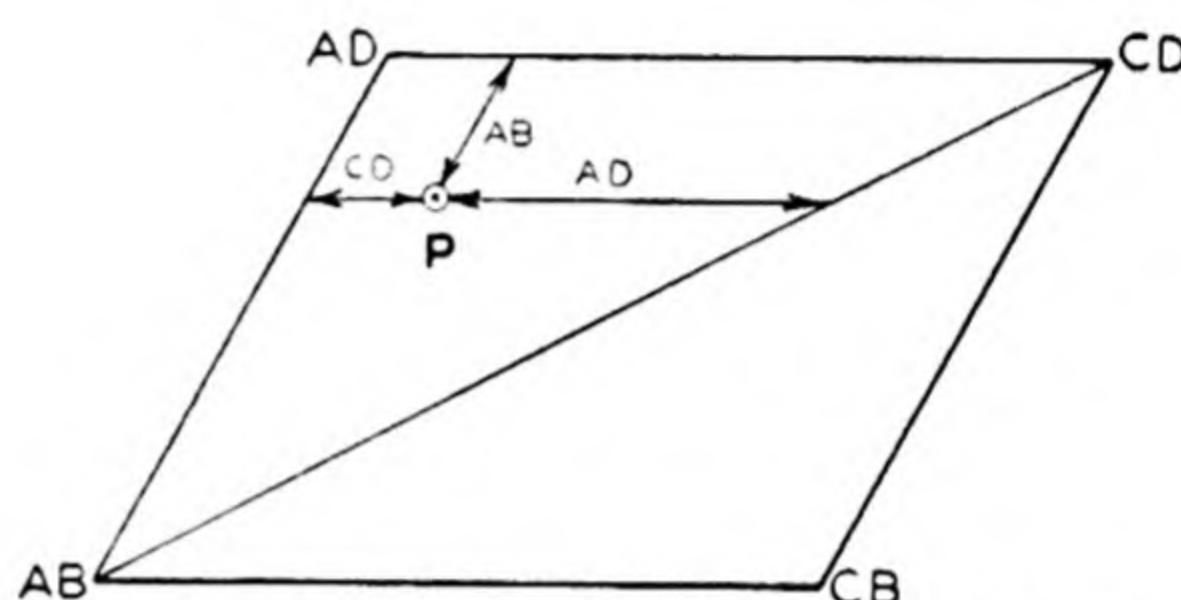


FIG. 15-2. Variation of Fig. 15-1.

unequal the two scales will differ, since each side is still the unit of 100%.

Fig. 15-1, moreover, is equivalent to the representation, on the horizontal axis, of the percentage of C in the total equivalents of A and C, and on the vertical axis, of the equivalent percentage of D in the total of B and D. The horizontal axis represents the proportion of the two positive or basic radicals or ions, and the vertical axis the proportion of the two negative or acidic radicals or ions (Fig. 15-3). Now there is no particular significance in a diagonal as part of the graphical apparatus, unless it is desired to translate these proportions into percentages of three actual substances taken as the components. The corners are still the same four substances and the components are still simply three of these substances. Although the diagram represents proportions of "ions" of the same sign, no point in the diagram represents an ion, which is merely a convenient mathematical concept from the point of view of the Phase Rule. We can add or subtract any of the three substances arbitrarily taken as the components, or we can arbitrarily change the ratio of any two; but we cannot add or subtract an ion, or even arbitrarily change the ratio of two ions, without changing the quantities and proportions of other ions. We here talk about ions as one way of expressing the meaning of the composition plane, but we do not in any way treat them as components. A diagram may be labeled with ions at its corners but it must be remembered, when the diagram is considered in connection with problems of solidification and precipitation, that what

is separating or dissolving is a substance, namely, a component or a compound of the components, not merely an "ion," and that tie-lines have no significance unless they join phases, which are never "ions." If a system consists entirely of so-called "ionic substances," the maximum number of components is one less than the number of ions.

[In this connection we may recall, from Chapter I, that a simple displacement system, $A + CD \rightleftharpoons AD + C$, is a ternary system. If the composition is limited to the four substances represented in the chemical reaction, the number of equivalents of D is limited to $\leq A + C$. If this restriction is removed, we have the general additive ternary system A-C-D, and a simple displacement system is seen to be always a part of an additive system, the region defined, for example, by the trapezoid A-AD-CD-C of Fig. 15-4(a) (cf. Figs. 12-(47-53)). But this region may also be plotted on

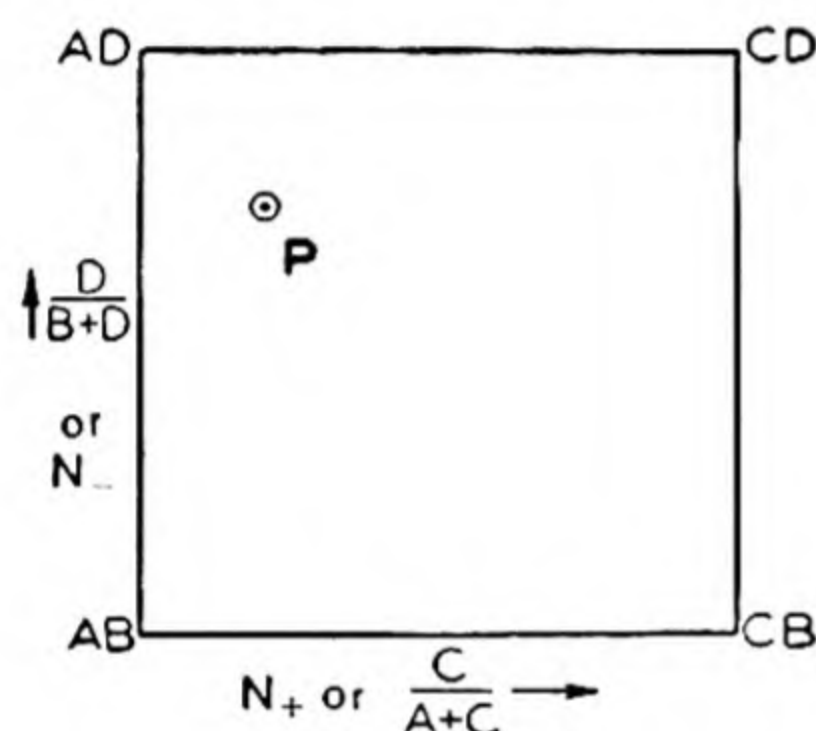
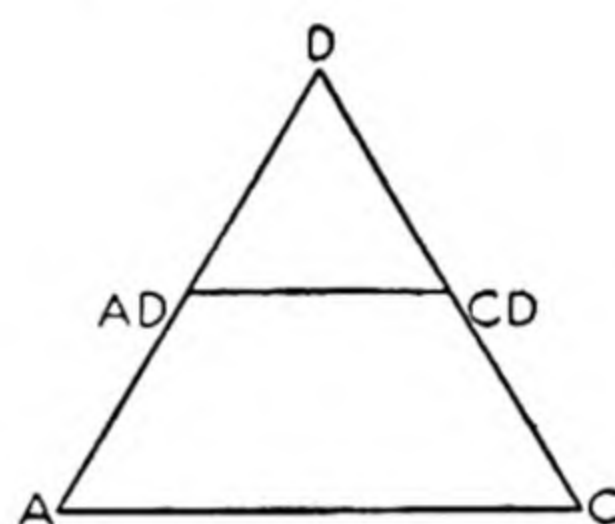
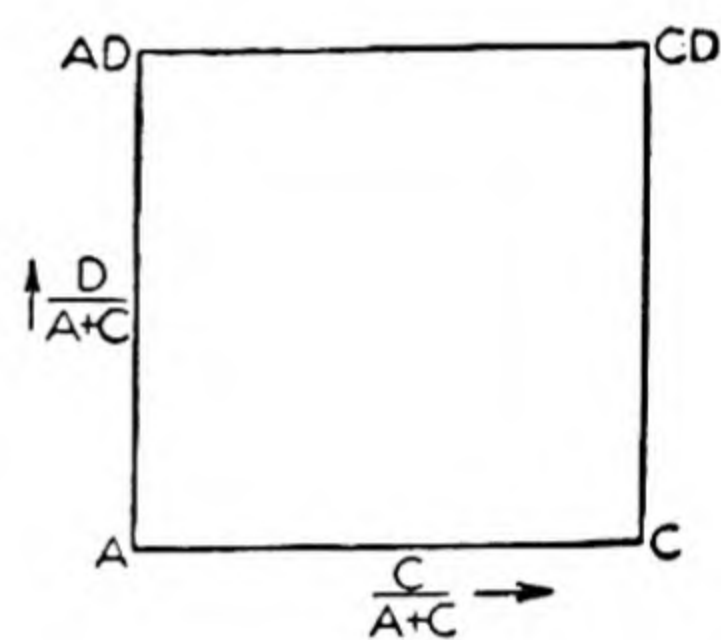


FIG. 15-3. Plotting in terms of radical proportions.



(a)



(b)

FIG. 15-4. Simple displacement system.

the square of Fig. 15-3, as in Fig. 15-4(b), whereupon we see the close relation between "simple displacement" and "double displacement" as two classes of the general reciprocal ternary system.]

Fig. 15-1 may also be considered as based on its diagonals as axes, as in Fig. 15-5(a), the unit now being half the diagonal, or O-CD, for 100%. Now if the components are still taken as AB, CD, and AD, a point P is plotted by measuring the equivalent percentage (number of equivalents per 100 equivalents of all three components) of AD on the $+y$ axis ($=aP$), and the number of equivalents of CD in excess of AB (per 100 total equivalents) on the $+x$ axis ($=bP$). The result has the same significance, that is, fixes the same point for the same composition, as the method shown in Fig. 15-1. Again compositions falling in the triangle AB-CD-CB require negative quantities of AD for their expression. Once plotted the composition of the point P in Fig. 15-5(a) can be read back from the diagram also in terms of Fig. 15-1, with the side rather than the half-diagonal as the unit, or on the basis of Fig. 15-3, in terms of radical ratios.

Like Fig. 15-2, Fig. 15-5 (a) need not have its axes intersecting at right

angles, nor need it have sides of equal lengths; the figure is still simple as long as it remains a parallelogram, provided that separate scales are then used for the pairs $AB + CD$ and $AD + CB$. But so long as there are two intersecting axes, one for each pair, the figure need not be a parallelogram, and it may have all four sides of unequal lengths (Fig. 15-5(b)). This dissymmetric type of figure may be used if it is found desirable for some special purpose to plot the number of equivalents of each substance not in

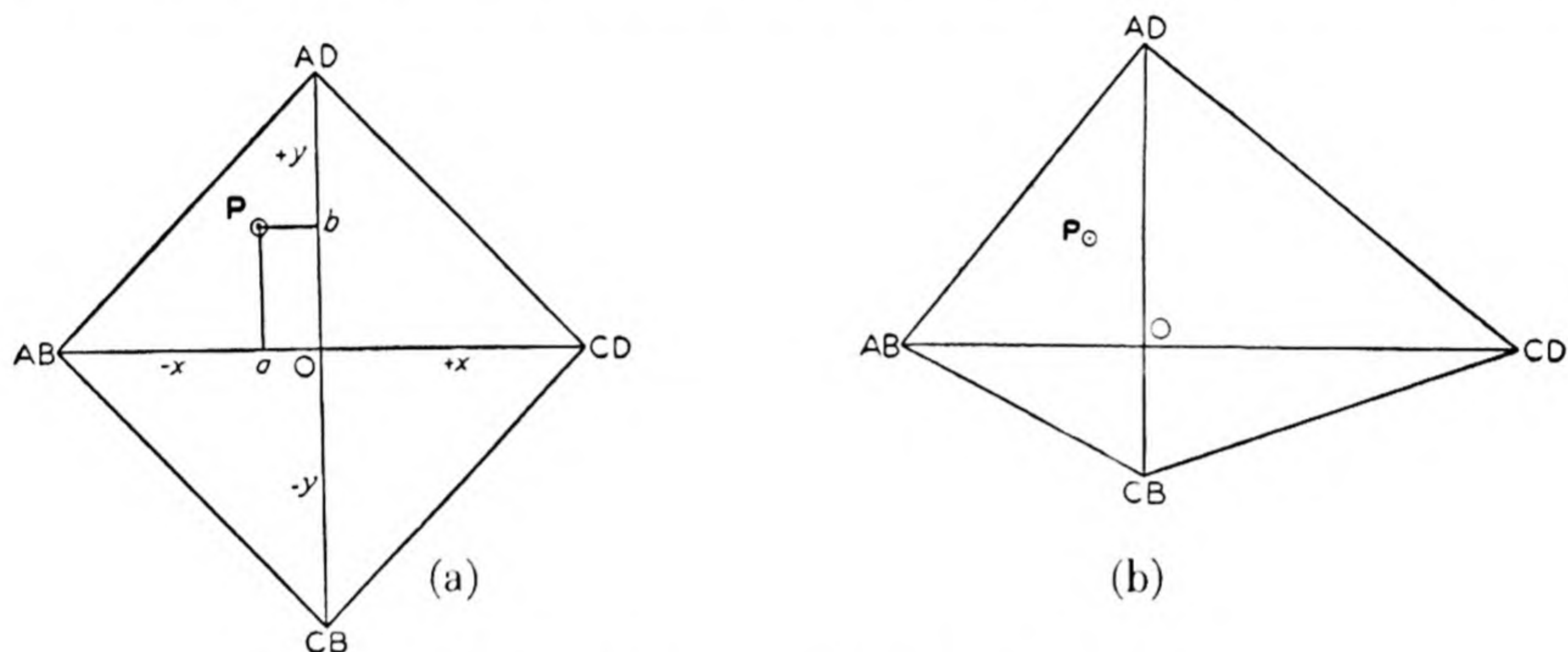


FIG. 15-5. Plotting on basis of diagonals.

100 equivalents of total but in some fixed total weight.¹ Then because the substances differ in their equivalent weights, the length of the line O-AD for one substance will not be equal to the lengths for the others. With a uniform scale for both axes (which need not intersect at right angles), the plotting is similar to that explained for Fig. 15-5(a). The composition of the plotted point, such as P, however, is now read in terms of weight percentage. With AB, CD and AD as the components, the triangle AB-AD-CD is treated as a composition triangle of the type of Fig. 10-2.

In every case, however, from Fig. 15-1 to Fig. 15-5, the usual principles of tie-lines, such as that of the center of gravity for calculating ratios of phases in equilibrium from the total composition, that of the convergence of tie-lines at the composition of a pure phase, and that of the crystallization paths on cooling, apply just as in the additive case. If the components are taken as AB, CD, and AD, addition or subtraction of any one of these substances, as by precipitation from a solution, causes the composition of the liquid to move on a straight line through the solid phase and the total composition, the ratio of the other two components remaining constant in the liquid. But the (inverse) segment ratio of the tie-line does not give the weight ratio of the phases but the ratio of the number of equivalents in the

¹ J. E. Ricci and C. M. Loucks, *J. Chem. Educ.*, **15**, 329 (1938).

phases, except in Fig. 15-5(b), which, with every point representing a unit weight of sample, gives the (inverse) weight ratio directly through the tie-line segments.

If all the phases involved in the "double decomposition" may be expressed additively (and positively) in terms of three oxides, then it may be more convenient to treat the system as merely part of the larger additive system of these three oxides. It is not surprising, of course, that metathesis should be representable in an "additive" system, for we have seen that one of the two types of invariant point (at constant P or T), the diagonal type or type B , is fundamentally a metathetical one, and this arises without the introduction of any chemical concept of "double decomposition," "ionic dissociation," etc.

For example, then, the system $\text{Bi}(\text{NO}_3)_3\text{-H}_2\text{O}$, involving the solid basic salt BiONO_3 , which may or may not be hydrated, may be represented as in Fig. 15-1, as a metathetical system, with the substances H_2O , $\text{Bi}(\text{NO}_3)_3$, and HNO_3 as the components AB , CD and AD respectively. Then the basic salt CB would have the composition $\text{Bi}(\text{NO}_3)_3 + \text{H}_2\text{O} - 2\text{HNO}_3$. But this system is usually represented as part of the system $\text{Bi}_2\text{O}_3\text{-H}_2\text{O-N}_2\text{O}_5$, whereupon not only these substances but even other possible phases are expressible as additive in positive terms of these oxides; Fig. 15-6 is the schematic 20° isotherm.²

When the acid is not an oxygen acid, as in the system $\text{Na}_2\text{O-HCl-H}_2\text{O}$ forming anhydrous NaCl as a solid phase, the system must be treated as a reciprocal ternary system; while the salt $\text{NaCl}\cdot 2\text{H}_2\text{O}$ is additive in terms of the base, acid, and water, the anhydrous salt must be considered as a compound of the base and the acid with a negative value of the water content, —its composition being $\text{Na}_2\text{O} + 2\text{HCl} - \text{H}_2\text{O}$.

If hypothetical oxides are assumed as the components, a great number of metathetical ternary systems could be treated in this way. But even if the oxides are real or known substances, the procedure would not in general be justifiable, even if mathematically correct. If the oxides of Fig. 15-6 are actually used to make up ternary mixtures, they give at equilibrium the phases shown. But this would not in general be true. For example, the hydrolytic equilibrium of potassium alcoholate and water, $\text{KOC}_2\text{H}_5 + \text{HOH} \rightleftharpoons \text{KOH} + \text{HOC}_2\text{H}_5$ (or similarly that of any ester and water) may be represented mathematically as part of a system of three oxides, here K_2O , $(\text{C}_2\text{H}_5)_2\text{O}$ and H_2O (Fig. 15-7). The rhombus' of a composition plane like Fig. 15-2 (with equal sides and 60° angle) is here part of an additive triangular system. But KOC_2H_5 is not formed by the mere mixing of K_2O

² As sketched in D. A. Clibbens (Ref. F), p. 164; from data (and diagrams) of G. M. Rutten and J. M. van Bemmelen, *Z. anorg. Chem.*, **30**, 342 (1902).

and $(\text{C}_2\text{H}_5)_2\text{O}$, nor alcohol from ether and water. The diagram would represent a false equilibrium. When actual double decomposition is involved, therefore, whether or not such mathematical additivity is possible, the

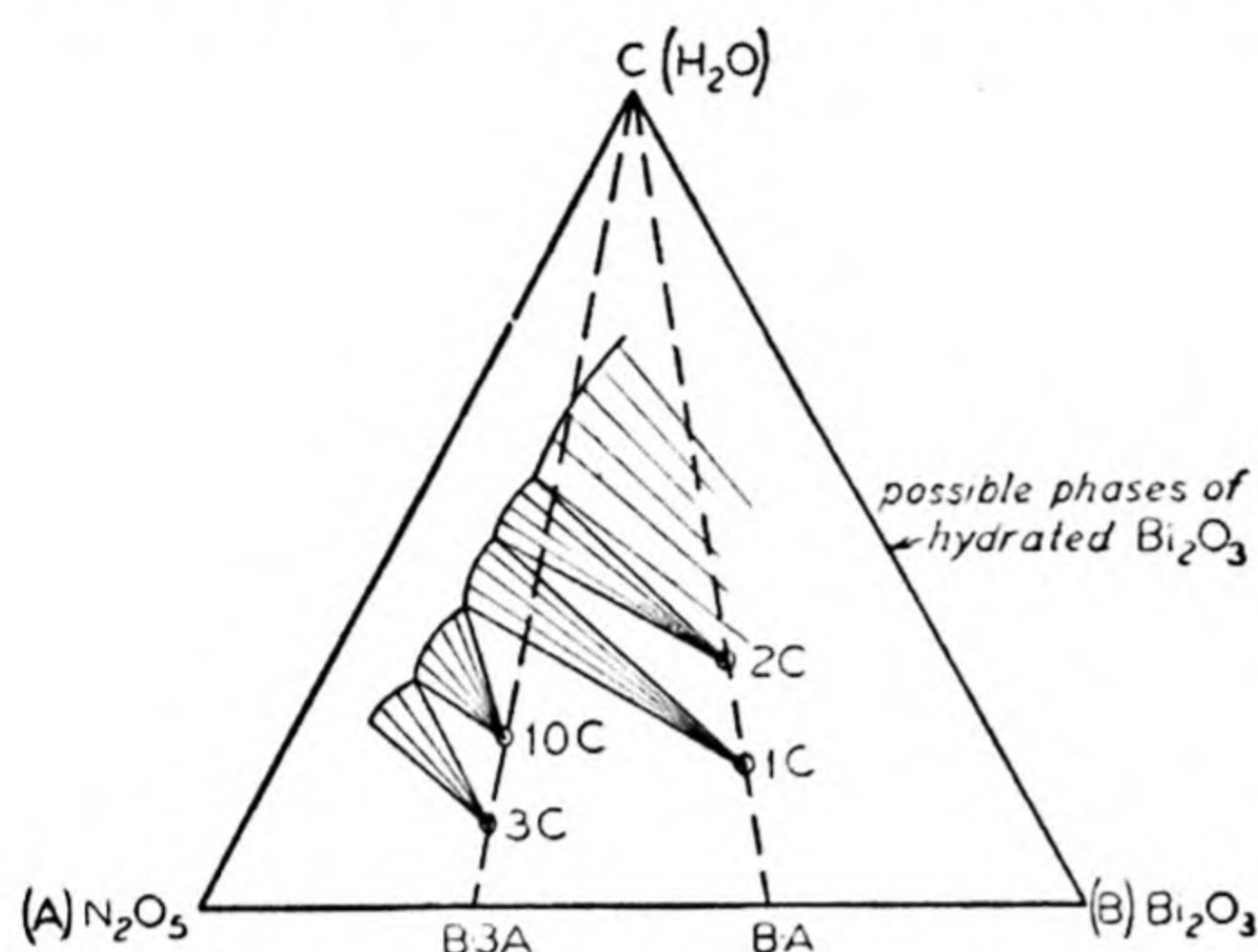


FIG. 15-6. Hydrolytic system as part of additive system.

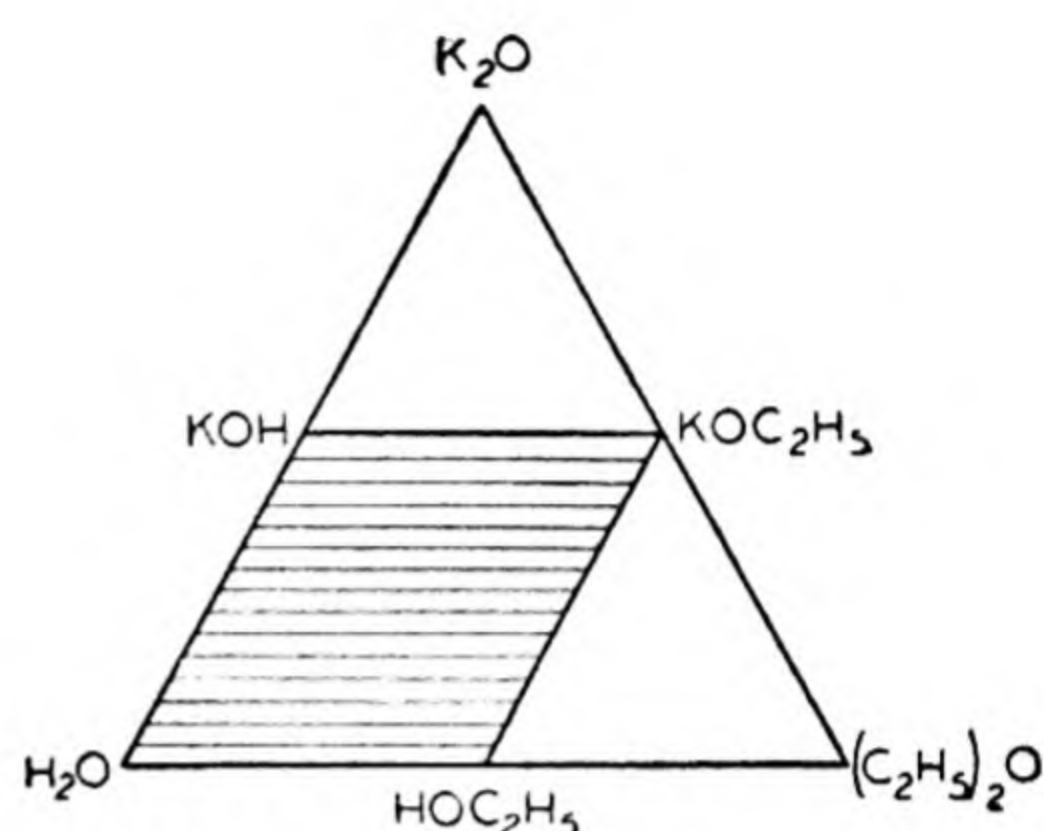


FIG. 15-7. Relation between reciprocal and additive system.

diagram of Fig. 15-1 (or one of its variations) is used. The usual cases encountered are the solvolysis of a salt or of an ester and the interaction of a reciprocal pair of salts in absence of solvent.

C. Example; Two Binary Solid Solutions

As a simple illustration, we shall consider an isotherm (schematic) for the system $\text{Na}_2\text{Cl}_2\text{--K}_2\text{SO}_4$ at 700° .³ This is, as usual, the isothermal section of the T/c prism of the ternary system (now a square prism). Each face of the prism is a binary system: NaCl--KCl , $\text{KCl--K}_2\text{SO}_4$, $\text{K}_2\text{SO}_4\text{--Na}_2\text{SO}_4$, and

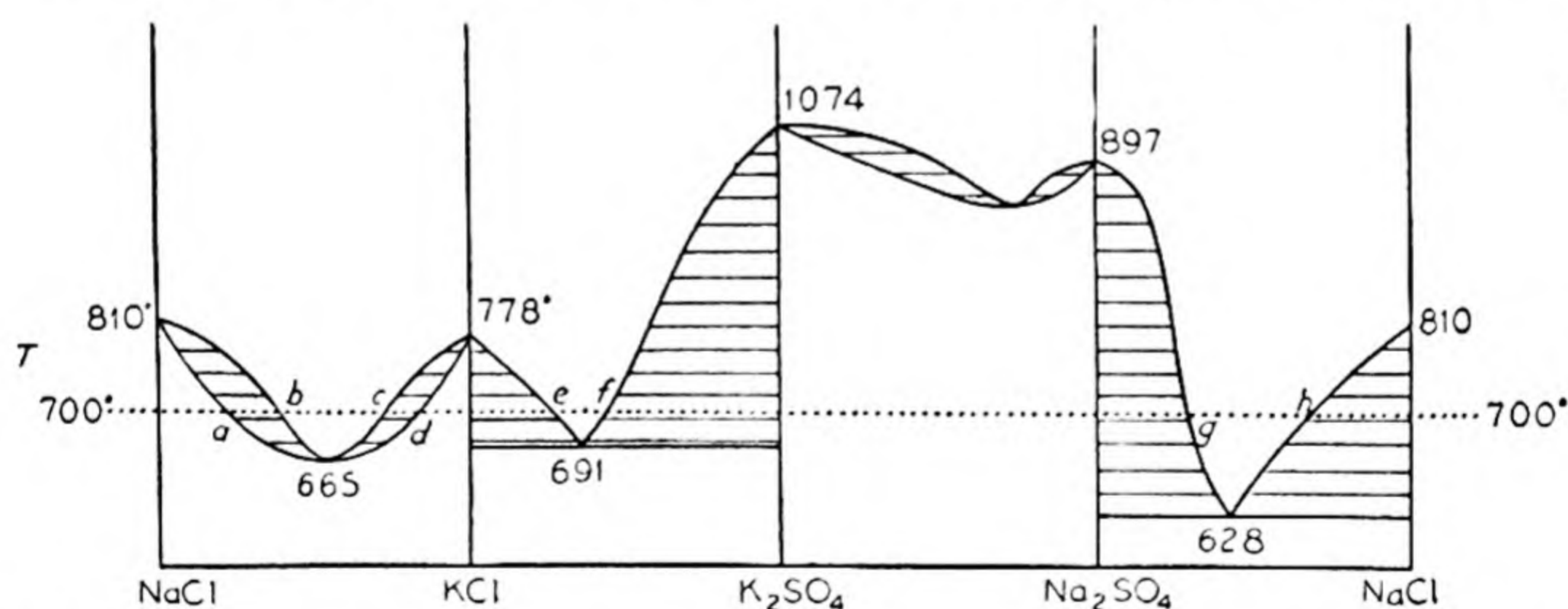


FIG. 15-8. The four binary diagrams of the reciprocal ternary system $\text{Na}_2\text{Cl}_2\text{--K}_2\text{SO}_4$.

$\text{Na}_2\text{SO}_4\text{--NaCl}$. These are shown side by side in Fig. 15-8. The second and fourth are simple eutectic systems, apparently involving the pure salts as solid phases at the melting point. The first and third have continuous solid

³ E. Jänecke, *Z. phys. Chem.*, **64**, 343 (1908).

solutions, with minima, at their melting points, although at room temperature NaCl and KCl show no measurable degree of solid solubility, and Na_2SO_4 and K_2SO_4 also form pure phases with the exception of a slight solubility of Na_2SO_4 in the compound glaserite. The 700° isotherm therefore involves a binary solid solution of the two chlorides containing no sulfates, and a binary solid solution of the sulfates containing no chlorides (Fig. 15-9(a)).

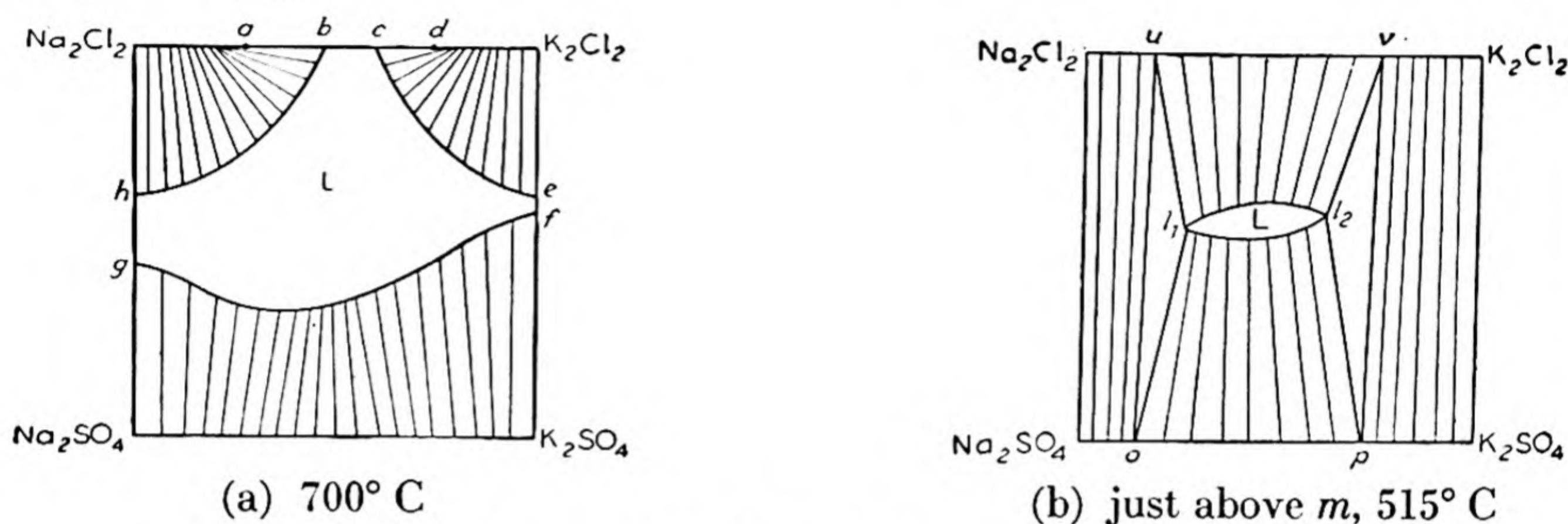


FIG. 15-9. Schematic isotherms of system $\text{Na}_2\text{Cl}_2\text{-K}_2\text{SO}_4$.

The formulas of the chlorides in the diagram are doubled since the composition is plotted in equivalents. The points a to h are parts of the binary systems and may be identified from Fig. 15-8. The curve gf is the solubility curve, at 700° , of the binary solid solution of the two sulfates in the ternary liquid, and the composition of this liquid at any point may be read either as in Figs. 15-1 and 15-5(a), in terms of three of the salts as components, or as in Fig. 15-3, in terms of the proportions of the ions, Na^+ and K^+ horizontally, and SO_4^- and Cl_2^- vertically. The tie-lines from the curve gf run to the whole of the binary side $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$, since the solid solution is continuous; these tie-lines tend to diverge somewhat at the solid solution end, if the miscibility gap is near. The curves hb and ce represent the solubility of the solid solution of the chlorides in ternary liquid. The curve does not run across the whole diagram because the temperature is above the minimum melting point of the solid solution. Solutions on hb are saturated with solid solutions with compositions ranging from NaCl to point a ; points a and b correspond to points x and y of Fig. 12-4(a).

The liquidus surface of the T/c prism will consist of two parts, the crystallization surface of the chloride solid solution and that of the sulfate solid solution, divided by a curve joining the two binary eutectic points. Since there is a minimum on the curve (at 515°), the projection of the crystallization surface will appear as in Fig. 15-10. For the separation of a pure solid phase the crystallization paths would be straight lines, as usual, but they are here curved; the crystallization end-point is the ternary minimum m . An

isotherm just above m would appear as in Fig. 15-9(b), somewhat as in the case of Fig. 12-6 and 12-7(a). The region Na_2Cl_2 - u - o - Na_2SO_4 is a 2-phase mixture of chloride solid solution and sulfate solid solution; the region v - K_2Cl_2 - K_2SO_4 - p is a similar mixture of two solid solutions. The solid solutions on the lines uv and op , on the other hand, are in equilibrium with liquid. The triangles ul_1o and pl_2v are isothermally invariant systems, and the liquids l_1 and l_2 are points on the eutectic curve of Fig. 15-10, one on each side of m . Just below m , the system consists of a mixture of two binary solid solutions for any composition, and the two outer regions of Fig. 15-9(b) merge into one tie-line field.

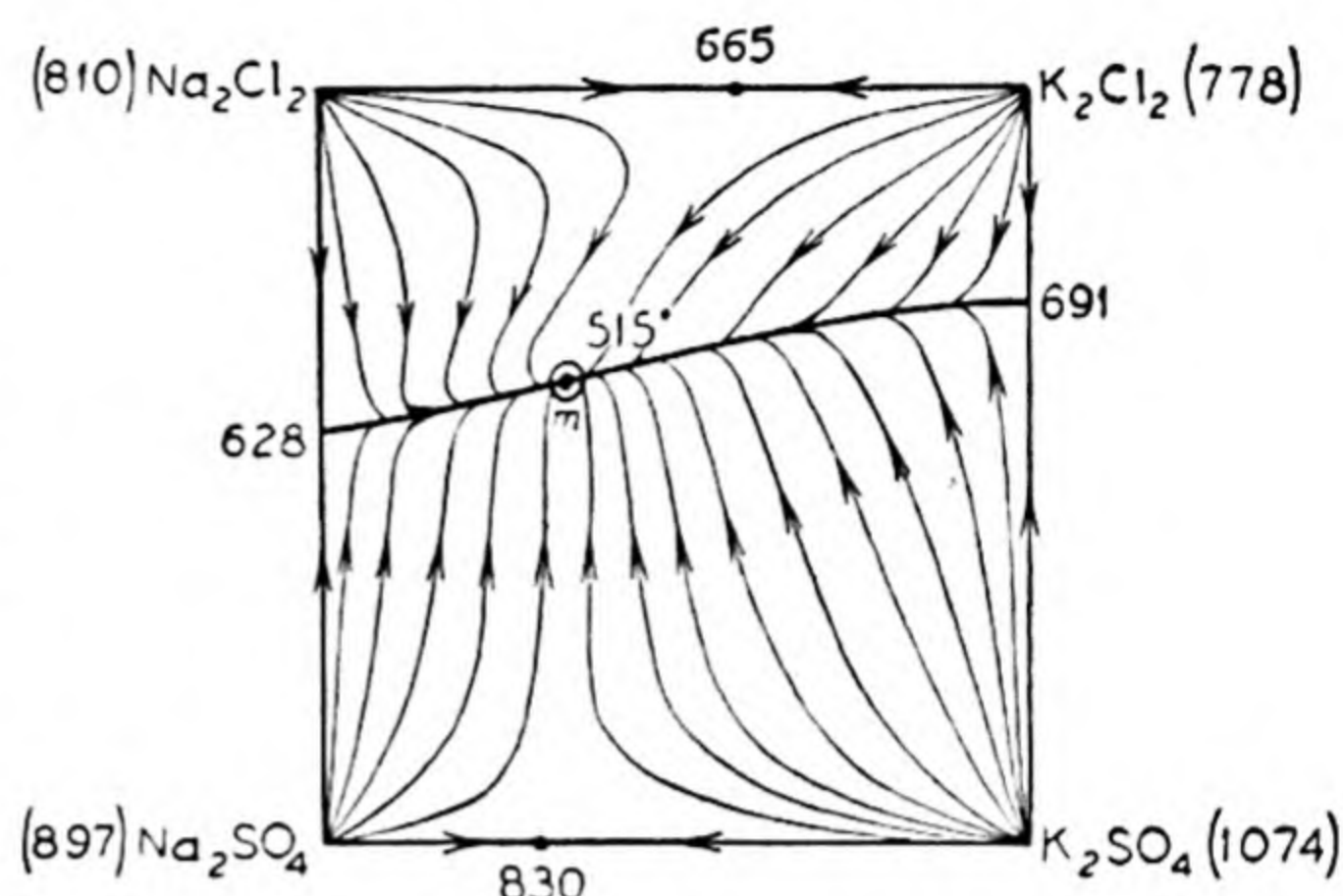


FIG. 15-10. Polythermal projection, system Na_2Cl_2 - K_2SO_4 .

D. Miscibility Gap in One of Two Binary Solid Solutions

If one binary (AD - CD) has limited solubility in the solid state, with a eutectic, and the opposite binary (AB - CB) has unlimited solid solubility,

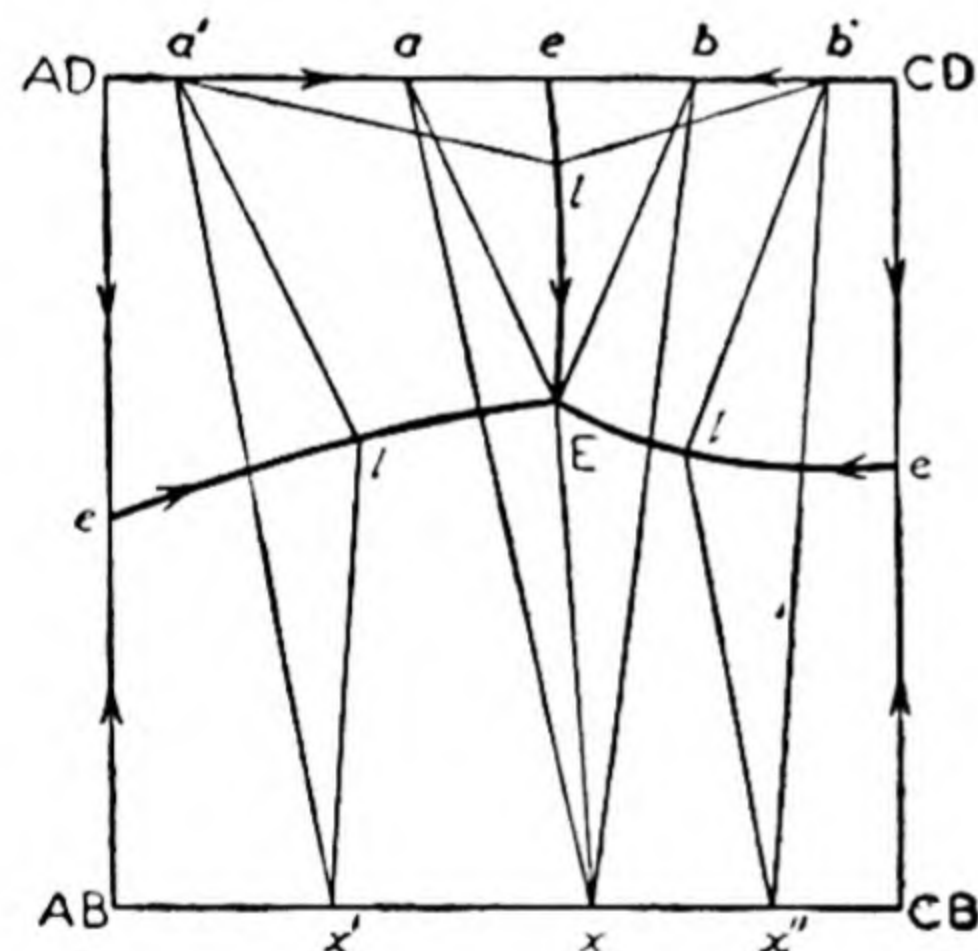


FIG. 15-11. Solid MG in system AD - CD , with eutectic.

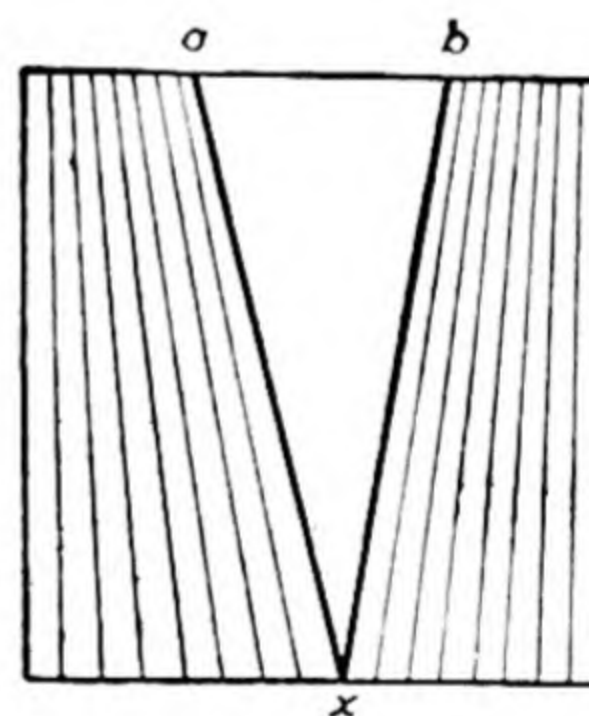


FIG. 15-12. Isotherm of Fig. 15-11, just below E .

there will be an invariant point in the crystallization surfaces, since three solid phases are possible. In Fig. 15-11 this invariant is assumed to be a ternary eutectic, with three curves of twofold saturation falling to it with respect to temperature; (but this is not the only possibility). The eutectic is the meeting of three equilibria $la'b'$, $la'x'$ and $lb'x''$. The eutectic triangle is abx , and the system just below the eutectic appears as in Fig. 15-12, so that compositions in the triangle abx solidify (with invariance at E) to a mixture of the three solids a , b , x .

E. Four Solid Phases

1. Pure Components as Solids

If four separate solid phases are possible in the system, at the melting point, there will be four fields of crystallization and two invariants. As usual, if all the curves of twofold saturation enter the T/c prism with falling T , one invariant must be a ternary eutectic, a congruent crystallization end-point with liquid lying inside the triangle of its three solids, while the other may be a peritectic, or an incongruent crystallization end-point for its three solids. The simplest case is that in which the four salts are all pure, with no solid solution at all. With two eutectics, as assumed in Fig. 15-13,

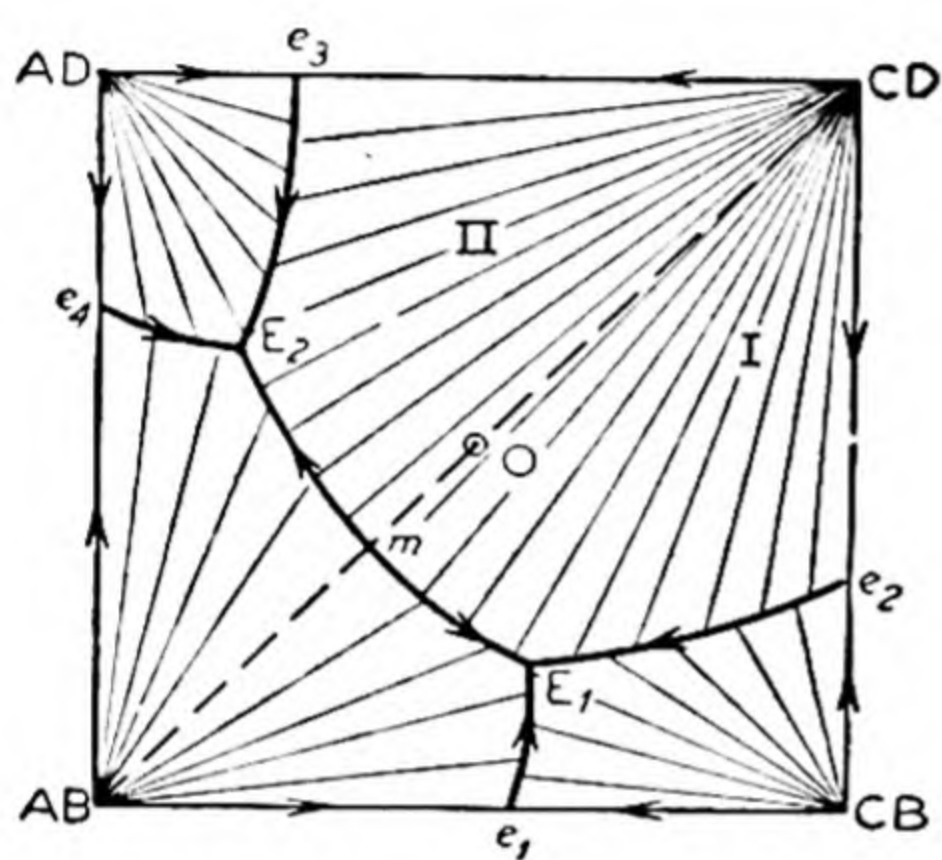


FIG. 15-13. System with four pure solids; polythermal projection.

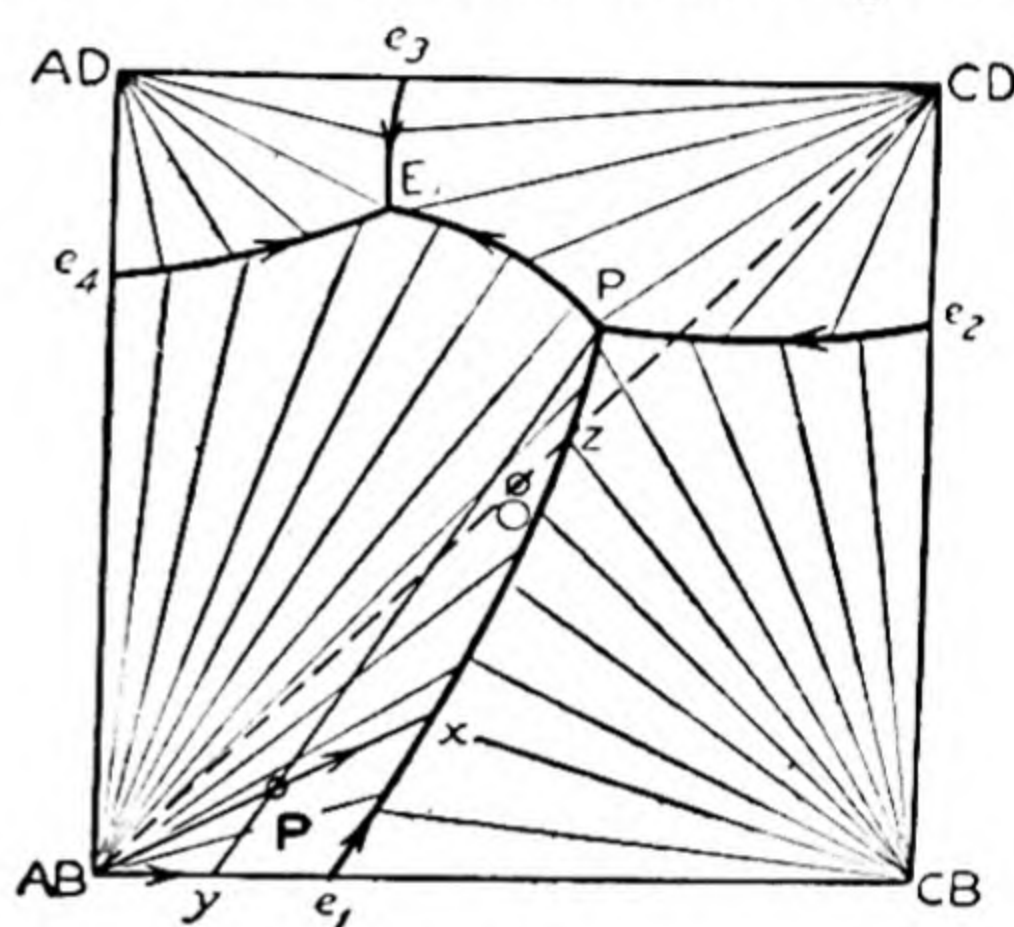


FIG. 15-14. Variation of Fig. 15-13.

the system is, at least at its melting point surface, the juxtaposition of two simple ternary systems, in this case AB-AD-CD and AB-CB-CD, since the section AB-CD is quasi-binary. The diagonal AB-CD, in other words, cuts the curve of liquid saturated with both AB and CD, and point m is a maximum (saddle point) on the curve E_1E_2 . Since, with pure solids, the crystallization paths are straight lines from the corners, the behavior of liquids falling anywhere in the diagram may be followed easily.

On complete solidification, then, we obtain either the mixture $AB + CD + CB$, for compositions in triangle I, or the mixture $AB + CD + AD$ for compositions in triangle II. The pair $AB + CD$ is therefore known as the **stable pair**, the reciprocal pair $AD + CB$ as the **unstable pair**, at the temperature of the crystallization surface. Hence the diagonal AB-CD is distinguished as the **stable diagonal**. Liquid saturated with the stable pair is possible, on the curve between the invariants, E_1E_2 , but liquid saturated with the unstable pair is not possible, at equilibrium.

If one of the invariants (P) falls outside the triangle of its three solids, as in Fig. 15-14, then P is a peritectic point, type B, and the incongruent

crystallization end-point for all liquids with original composition in triangle I, since these liquids must solidify to a mixture of the three solids $AB + CD + CB$. Except for the position of the point P, the structure of the T/c prisms of which Figs. 15-13 and 15-14 are the polythermal projections, is essentially the same (Fig. 15-15). This figure resembles both

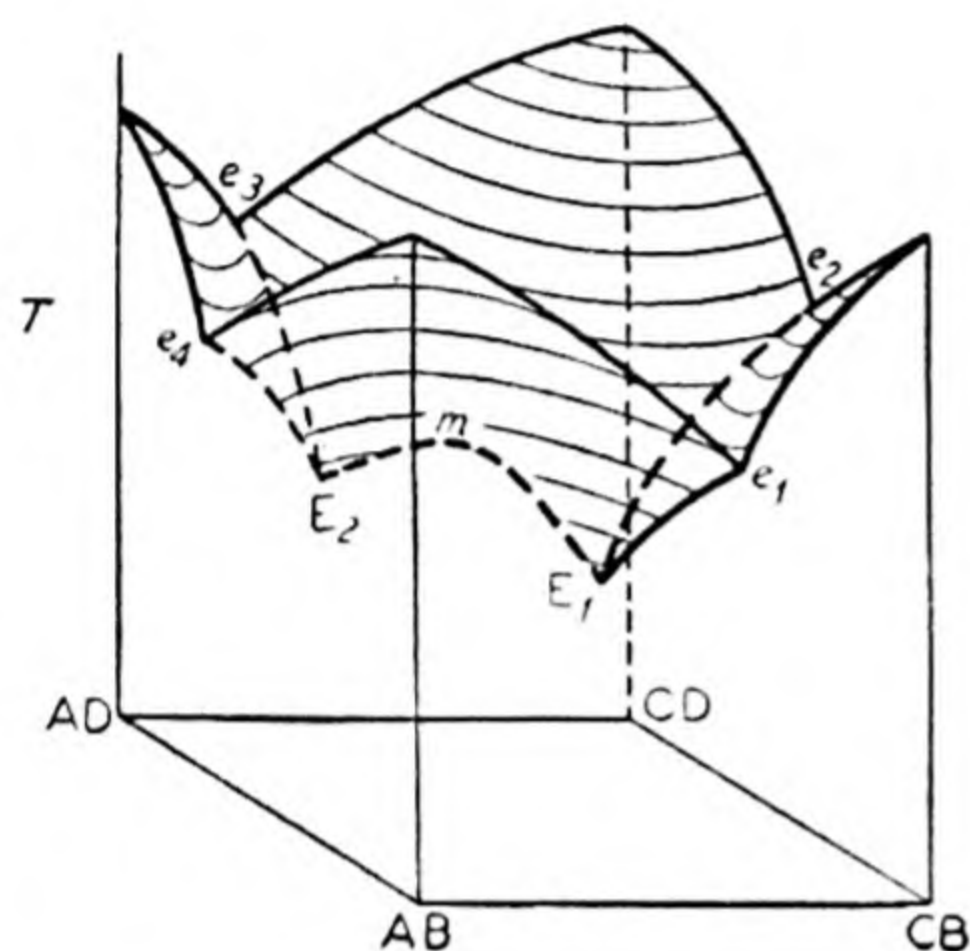
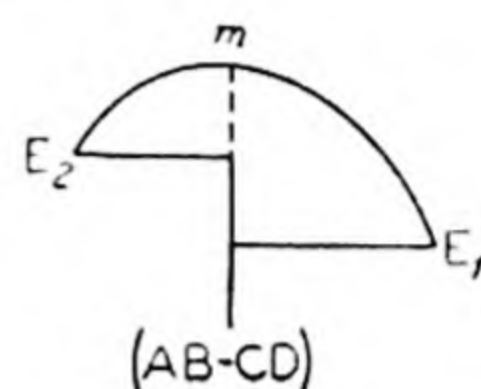
FIG. 15-15. T/c prism for Fig. 15-13.

FIG. 15-16. Detail of Fig. 15-15.

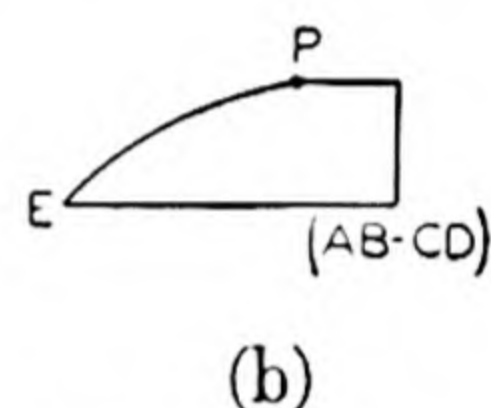
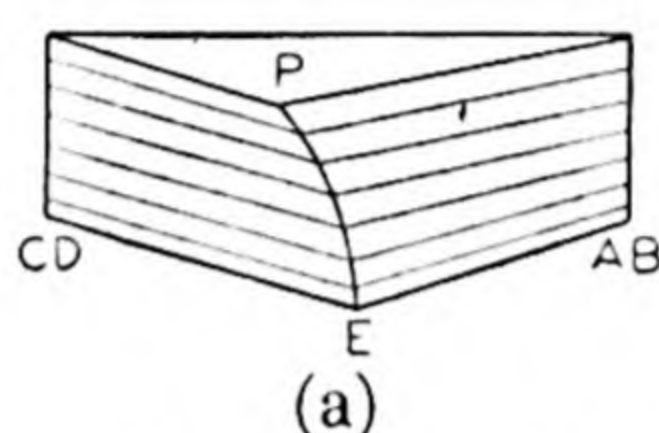


FIG. 15-17. Details of Fig. 15-14.

Fig. 12-16 and, particularly, Fig. 12-26. Each of the four solubility surfaces is connected by horizontal tie-lines to the vertical line representing the pure salt, these tie-lines describing a space of the nature of Fig. 12-19. The four curves e_1E_1 , e_2E_1 , e_3E_2 , e_4E_2 , are the edges of spaces of the form of Fig. 12-20, generated by 3-phase triangles. The curve E_1mE_2 is the edge of another such space, for the solids $AB + CD$. In outline, viewed from AB to CD, this space appears as in Fig. 15-16, if $E_2 > E_1$ in temperature. For the case of Fig. 15-14, the curve EP is the edge of the space pictured in Fig. 15-17: in Fig. 15-17(a) from the direction of AD, and in Fig. 15-17(b) as an outline, comparable to Fig. 15-16.

In either case, Fig. 15-13 or Fig. 15-14, the stable pair is $AB + CD$, which can saturate simultaneously the liquids on the curve E_1E_2 or EP. In Fig. 15-13 the melting of a mixture of AB and CD begins invariantly at the temperature of m (which, as a saddle point on curve E_1E_2 , is the eutectic of the quasi-binary system AB-CD) until one of the solids is consumed. An equivalent mixture (point O) leaves liquid + excess CD. In reverse a melt of an equivalent mixture, again point O, of the pair $AD + CB$, gives first CD on cooling and finally a mixture of $AB + CD$, the final liquid to solidify being the point m . In Fig. 15-14, the equivalent melt of AD and CB (point O) gives AB as primary crystallization product and then CB in addition when the liquid reaches point z on the curve e_1P . Further cooling leads to the ternary peritectic P, where CD begins to precipitate. Since the final composition must be point O, on the diagonal AB-CD, both the liquid

(point P) and the solid CB will disappear together (assuming equilibrium to be maintained to the end) to leave a mixture of the stable pair AB + CD. The unstable pair, in equivalent proportions, can therefore be transformed completely to the stable pair through the liquid phase.

A liquid of composition P, Fig. 15-14, produces AB when cooled to the AB crystallization surface, or the field AB- e_1 -P-E- e_4 . During precipitation of AB the liquid proceeds on the straight line AB-P to the point x on the curve e_1 P, when CB begins to precipitate. As the two salts are formed together, the liquid follows the curve to P, and, when P is reached, the solids are a mixture of AB and CB in the proportion y , on the line y PP. Now the system becomes invariant, and CD begins to precipitate. The temperature remains constant during the reaction $L + CB \rightarrow AB + CD + \text{cals.}$ until the liquid is all consumed. During the process the composition of the solid mixture, now including CD, moves on the line y P to the point P, leaving a mixture of AB, CD, and CB with the total composition P. If the original liquid fell in the region AB- z -P, or in triangle II, the invariance at P would last until the solid CB were all consumed, and the liquid, then saturated with AB and CD alone, would proceed to the eutectic E to give the mixture AB + CD + AD. Point P is therefore a diagonal type of invariant (type B), reached by all compositions in the quadrangle AB-P-CD-CB.

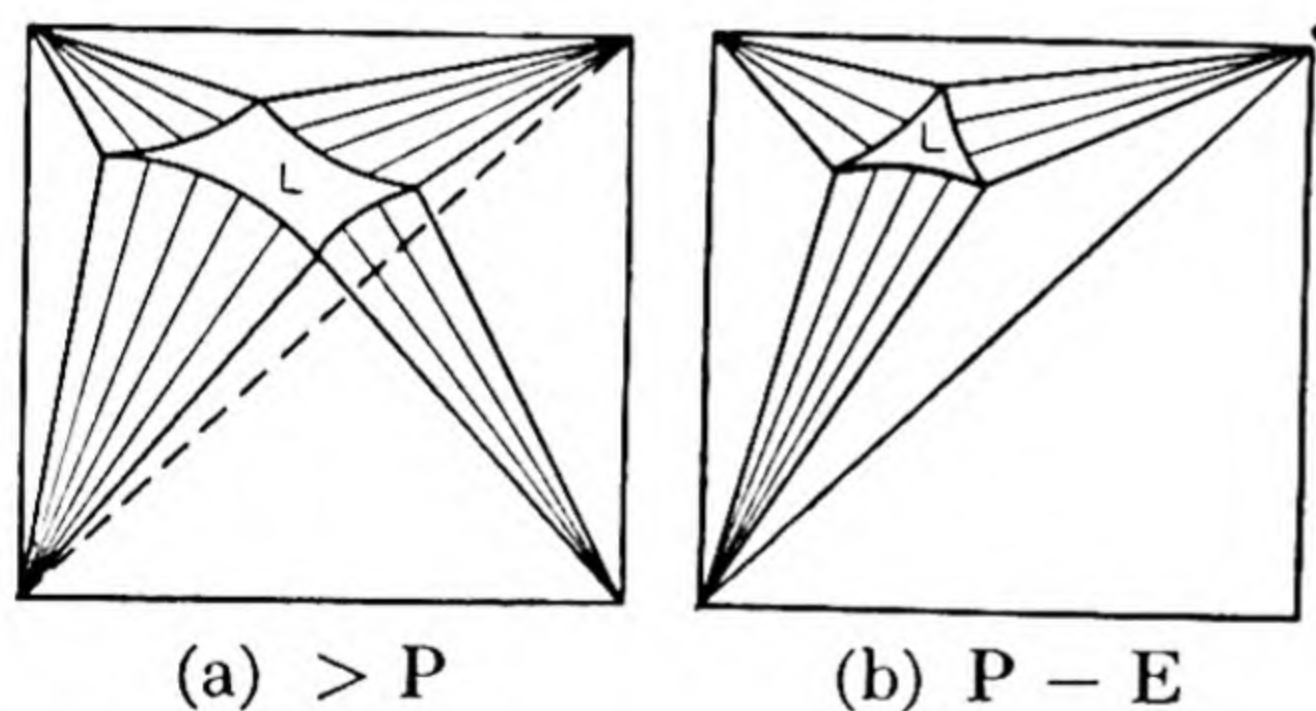


FIG. 15-18. Isotherms of Fig. 15-14.

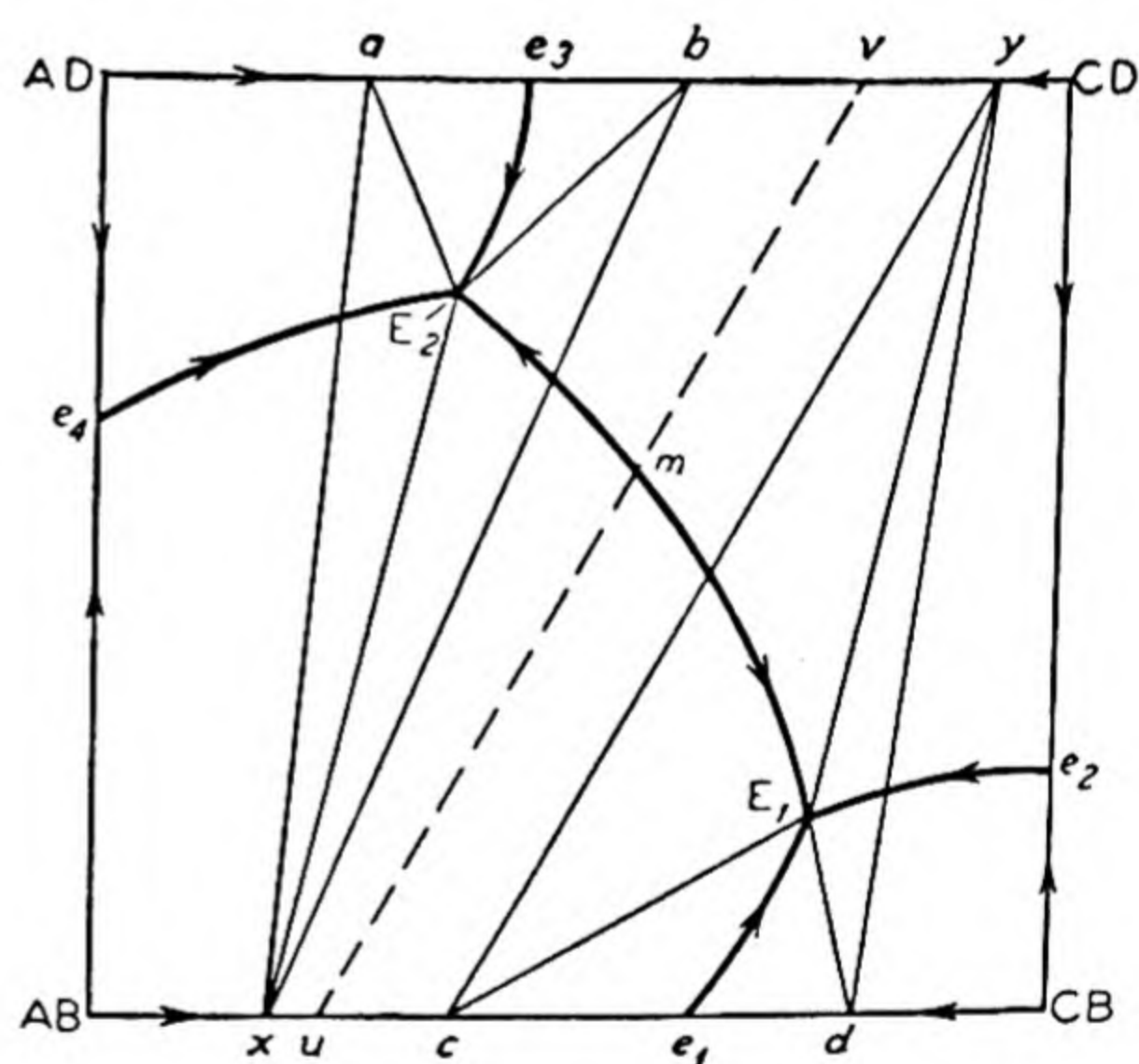


FIG. 15-19. System with four solid solutions; polythermal projection.

Two isotherms of Fig. 15-14 are shown in Fig. 15-18, one just above the temperature of P, the other just below.⁴

2. Four Solid Solutions

The essential features of this discussion are not changed if the four solid phases are solid solutions. There will be four solids, provided that no binary system forms continuous solid solution at the melting point. Still assuming

⁴ On Figs. 15-13 to 15-18, see E. Jänecke, *Z. phys. Chem.*, **64**, 305 (1908).

a eutectic in each binary, we now have Fig. 15-19, in which limited binary solid solution is assumed in the systems AD-CD and AB-CB. It is also assumed, for simplicity, that both ternary invariants are eutectics, and that the miscibility gaps do not change between the binary eutectics e_1 and e_3 and the ternary eutectics E_1 and E_2 . The limiting solid solutions in the AD-CD system are a and b , those in the AB-CB system c and d . The eutectic triangle abx is similar to that in Figs. 15-11 and 15-12, point x being a particular composition of the AB- c solid solution; the eutectic triangle cdy is, of course, a similar one, the point y being a particular composition of the b -CD solid solution. The eutectic E_2 is approached from high T by three systems of liquid of twofold saturation. One starts as the binary 3-phase line AD- e_4 -AB and proceeds to E_2 as a 3-phase triangle in the usual way, ending as the triangle aE_2x . Another starts as the binary line ae_3b , and ends as the triangle aE_2b . The third involves a solid solution in the range b -CD and one in the range AB- c . It starts as a 3-phase colinear equilibrium passing through the saddle point m , the point of temperature maximum on the curve E_1E_2 , since this is the curve of liquid simultaneously saturated with such solid solutions. From a 3-phase tie-line such as umv , therefore, with v between b and y and u between x and c , the 3-phase equilibrium falls on either side to the eutectics E_1 and E_2 , ending as the triangle bE_2x at E_2 and as the triangle yE_1c at E_1 .

On complete solidification, compositions in the region AD- a - x -AB give a mixture of two binary solid solutions, one on AD- a and one on AB- x ; those in b - yc give two solid solutions, one on by and one on cx ; similarly those in y -CD-CB- d give a mixture of two binary solid solutions. Those

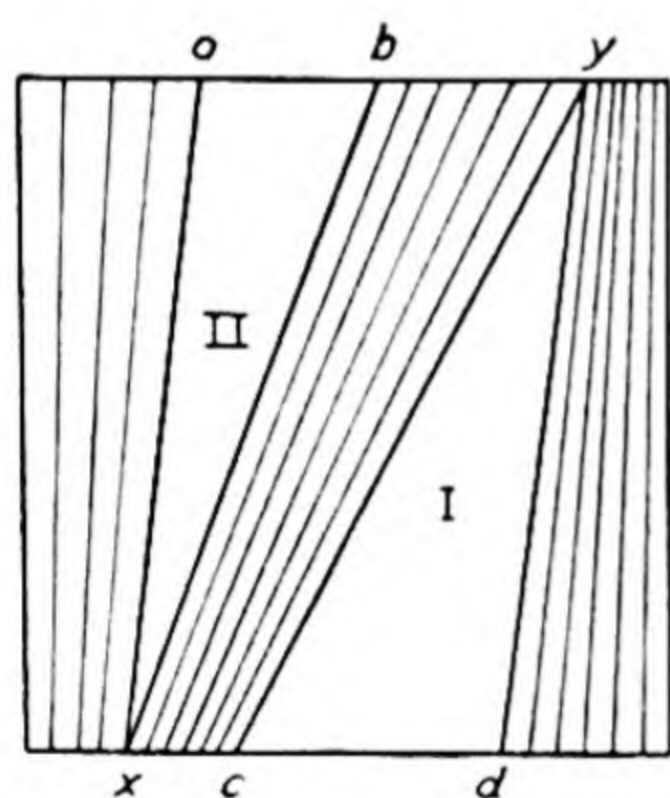


FIG. 15-20. Isotherm of Fig. 15-19, below eutectics.

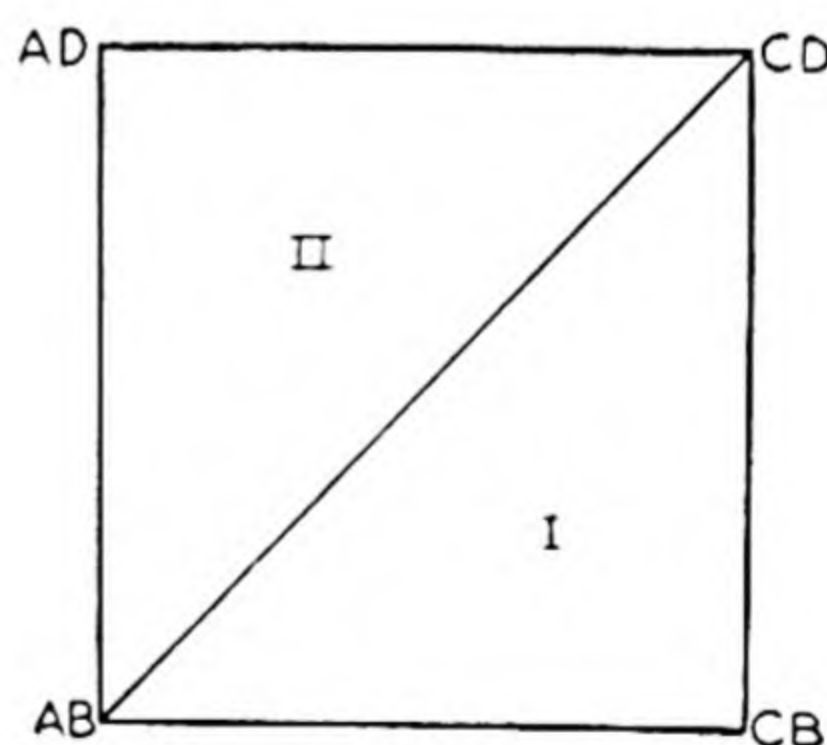


FIG. 15-21. Isotherm of Fig. 15-13 below both eutectics, or of Fig. 15-14 below the eutectic.

in the eutectic triangles give three phases, abx and ycd at E_2 and E_1 , respectively. Fig. 15-20 is an isotherm below both eutectics. This is to be compared with the system of Fig. 15-13 just below its eutectics, or Fig. 15-21. In this the stable salt pair is AB+CD; in Fig. 15-20 the stable solid solution pair is also "AB" (that is, solid solution xc) and "CD" (solid solution, by).

F. Stability of Pairs

With further lowering of temperature, however, a reversal of the stability of the pairs becomes possible, occurring at a 4-phase (isobaric) invariant point of the diagonal type *B*, the transition point in respect to the stability of the pairs. In Fig. 15-21 this involves merely a shift from *AB-CD* to *AD-CB* as the stable diagonal of the diagram, in the invariant reaction $AB + CD \rightarrow AD + CB + \text{cals.}$ In Fig. 15-20 it means that the 2-phase region solid solution *by* + solid solution *xc* becomes narrow, and vanishes

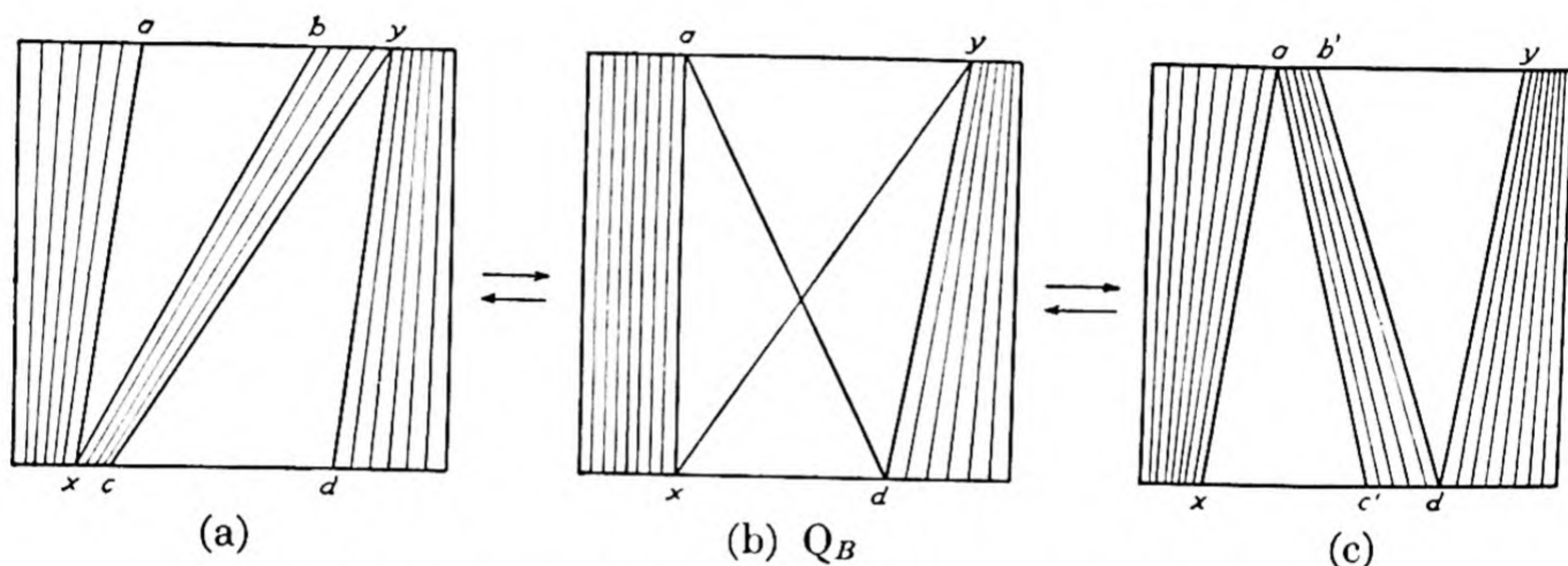


FIG. 15-22. Reversal of pair stability for system of Fig. 15-19.

as a line, to be replaced at the transition temperature by a line from *a* to *d* which itself then develops as a 2-phase region (Fig. 15-22). The reaction at the transition temperature in this case is $y + x \rightarrow a + d + \text{cals.}$

Such a reversal of the stability of pairs may conceivably also occur for the solids in equilibrium with liquid, or at the freezing point surface of the system, as a result of change in pressure in the 4-dimensional relations of the system. If we imagine such an effect, the isobaric freezing point diagrams (polythermal projections of the isobaric T/c prism of Fig. 15-15) would undergo the changes shown in Fig. 15-23. Each of these diagrams represents the freezing point relations at a different pressure. At the pressure of Fig. 15-23(a) the pair $AB + CD$ is stable and the section *AB-CD* is quasi-binary since the stable diagonal cuts the curve of liquid saturated with the stable pair. This curve becomes shorter as *P* changes, so that beyond Fig. 15-23(b) the system no longer has a quasi-binary section. At the pressure of Fig. 15-23(c) the curve vanishes to give a liquid saturated with four solids. This is an invariant, quintuple point of the system, at which the pair stability is reversed. Beyond this pressure the opposite pair becomes stable, and the isobars continue as shown in Figs. 15-23(d) and 15-23(e).

If the square diagrams of Fig. 15-23 are made trapezoidal, it is clear that

these relations apply equally for the simple displacement system, $A + BC \rightleftharpoons AC + B$, discussed in section D of Chapter XII, especially under Fig. 12-53.

The determination of the freezing points of known compositions of such salt systems establishes the crystallization (liquidus) surfaces and the curves and points of their intersections. The determination of the nature of the solid phases involved is possible through the study of crystallization paths and by means of the other methods mentioned in section A of Chapter XIII. The determination of the relations of the solids below the temperature of the liquidus surfaces requires knowledge of the four binary systems

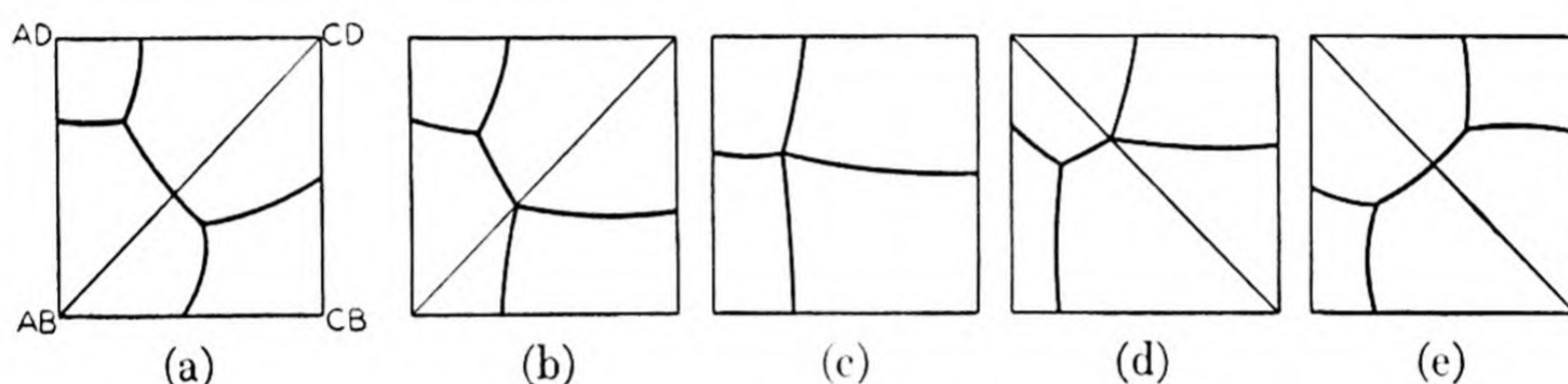


FIG. 15-23. Reversal of pair stability in equilibrium involving liquid.

and study of reactions in the solid state. If high temperatures are involved, this necessitates establishment of equilibrium usually directly from the solid salts, below their melting points, then quenching, and finally X-ray examination to identify the solids and to determine the extent of formation of solid solution. In this way the stability of reciprocal salt pairs has been related to some extent to the lattice energies, expressed approximately in terms of lattice parameters, of the crystals in pairs, with interesting correlations in groups of related systems, such as the alkali halides. In these salts⁵ that pair is stable which has the higher average cube edge and also the higher sum of heats of formation.

If the salts are soluble in water, and if they saturate the aqueous solution as anhydrous salts, then the equilibrium relations of the salts at low temperature are much more easily studied through quaternary solubility work. This gives information on the relative stability of salt pairs and on their solid solutions, at least within the range of measurable solubility relations. This is similar to what was pointed out in Chapter XIII, that the phase relations of the binary system of two solids below their melting points may be studied through ternary solubility isotherms involving aqueous or other solutions.

⁵ F. B. Thomas and L. J. Wood, *J. Am. Chem. Soc.*, **58**, 1341 (1936).

G. Compounds

The system $\text{K}_2\text{Cl}_2\text{--MgSO}_4$, shown in Fig. 15-24, is an example of a reciprocal salt system involving compounds both binary and ternary.⁶ The systems $\text{K}_2\text{Cl}_2\text{--K}_2\text{SO}_4$ and $\text{MgCl}_2\text{--MgSO}_4$ are simple eutectic systems. The other two binary systems involve the congruently melting compounds X, or $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ (langbeinite), and Y, or $\text{K}_2\text{Cl}_2 \cdot 2\text{MgCl}_2$ (anhydro-carnallite). The ternary compound Z, or $\text{K}_2\text{Cl}_2 \cdot 2\text{MgSO}_4$ (anhydro-kainite) is known as a tetragene salt⁷ since it contains four ions. This compound melts congruently (has an open maximum) at 920° . All the 3-solid invariants except point P are ternary eutectics, congruent solidification end-points

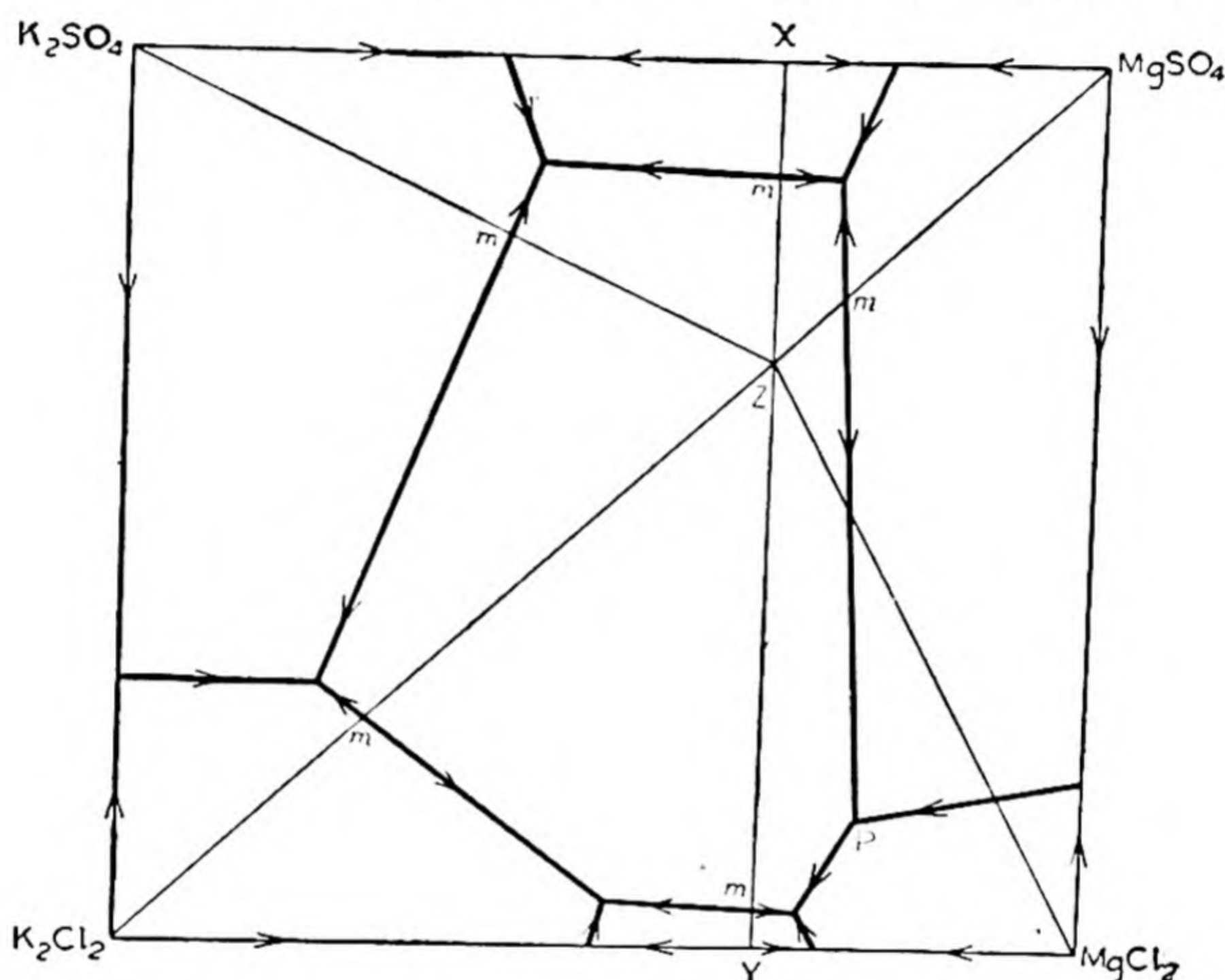


FIG. 15-24. System $\text{K}_2\text{Cl}_2\text{--MgSO}_4$; polythermal projection.

for their respective triangles. Point P is peritectic, and an incongruent crystallization end-point for melts with compositions in the triangle of its three solids, MgCl_2 , MgSO_4 , and $\text{K}_2\text{Cl}_2 \cdot 2\text{MgSO}_4$. There are five saddle points (m), and five quasi-binary sections, namely, those from anhydro-kainite to all the other solids except MgCl_2 . In addition, the section $\text{K}_2\text{Cl}_2\text{--MgSO}_4$ is a (condensed) quasi-binary section, with $\text{K}_2\text{Cl}_2 \cdot 2\text{MgSO}_4$ as a quasi-binary compound of congruent melting point.

H. Solvolytic Equilibria

For solvolytic equilibria, we shall take first an example discussed by Schreinemakers.⁸ Fig. 15-25 is the system potassium alcoholate-water

⁶ E. Jänecke, *Z. phys. Chem.*, **80**, 1 (1912).

⁷ W. Meyerhoffer, *Z. anorg. Chem.*, **34**, 145 (1903).

⁸ In Ref. P, Vol. III, Part 2; credited to A. J. C. de Waal, *Dissertation*, Leiden, 1910.

at 30° (schematic, and partly hypothetical in the vicinity of point b). Point a is the solubility of KOC_2H_5 in alcohol, g that of $\text{KOH}\cdot 2\text{H}_2\text{O}$ in water. The curve ab is the solubility curve of KOC_2H_5 , the solution becoming saturated also with $\text{KOH}\cdot 2\text{H}_2\text{O}$ at point b . The solubility curve of $\text{KOH}\cdot 2\text{H}_2\text{O}$ is interrupted into two parts, gf and eb , by a 2-liquid region, the binodal curve ekf . The triangle KOC_2H_5 - b - $\text{KOH}\cdot 2\text{H}_2\text{O}$ is isothermally invariant, consisting of liquid b and the two solids, the triangle e - f - $\text{KOH}\cdot 2\text{H}_2\text{O}$ is similarly isothermally invariant, consisting of solid and

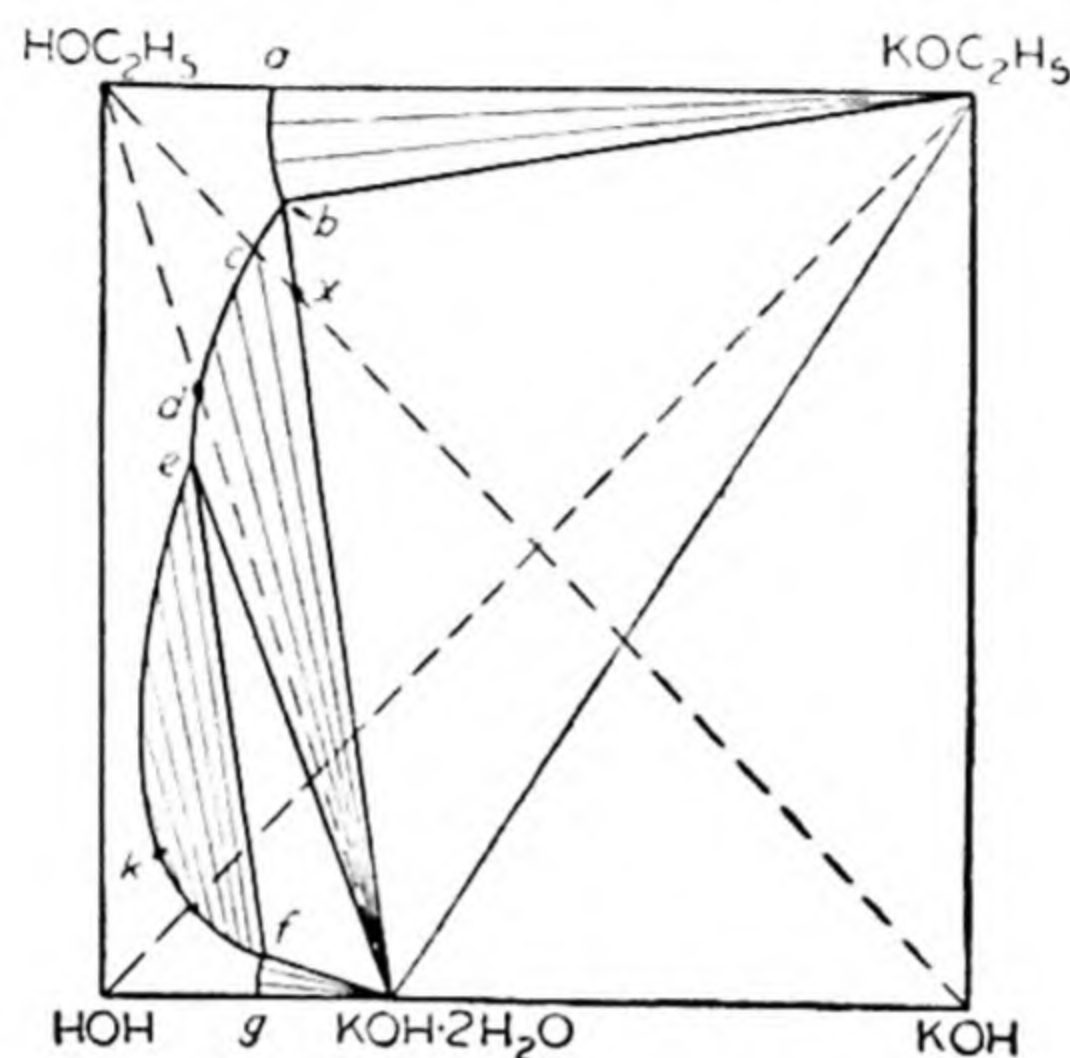


FIG. 15-25. Isotherm at 30° , system potassium alcoholate-water.

two liquids; and there is also a triangle of three solids, KOH - $\text{KOH}\cdot 2\text{H}_2\text{O}$ - KOC_2H_5 . If KOH is added to alcohol, an unsaturated solution is obtained until the point c is reached, on the solubility curve of the hydrate, and the alcohol becomes saturated not with KOH but with the hydrate. This means that there has been double decomposition to produce water for the hydrate, and that the solution must be said to contain potassium alcoholate. As the hydrate is precipitated upon continued addition of KOH , the solution in fact travels on the curve cb toward b . When the total composition reaches point x , solid KOC_2H_5 appears, and the solution now remains constant in composition during the continued addition of KOH , which is consumed in the chemical reaction, liquid (that is, alcohol) + $\text{KOH} \rightarrow \text{KOH}\cdot 2\text{H}_2\text{O} + \text{KOC}_2\text{H}_5$, until the liquid is all consumed. This occurs when the total composition enters the triangle KOH - $\text{KOH}\cdot 2\text{H}_2\text{O}$ - KOC_2H_5 , whereupon excess of KOH remains unchanged as a solid phase. In reverse, addition of alcohol to KOH causes immediate double decomposition, producing the new solid phases $\text{KOH}\cdot 2\text{H}_2\text{O}$ and KOC_2H_5 , until the KOH is all consumed and solution b appears.

Similarly, addition of water to KOC_2H_5 causes double decomposition, water + $\text{KOC}_2\text{H}_5 \rightarrow$ liquid b (that is, alcohol) + $\text{KOH}\cdot 2\text{H}_2\text{O}$, producing liquid b and $\text{KOH}\cdot 2\text{H}_2\text{O}$ until the KOC_2H_5 is all consumed, leaving the

be congruently soluble in water, their solubilities being given by points y and x respectively. Provided the binodal curve $fk g$ does not reach the lines H_2O-y and H_2O-x , the sections H_2O-D_1 and H_2O-D_2 are quasi-binary, and the triangles $H_2O-HOC_6H_5-D_1$, $H_2O-D_1-D_2$ and $H_2O-D_2-D_3$ constitute separate quasi-ternary isotherms. The addition of KOC_6H_5 to water therefore involves no double decomposition, at least up to the total composition D_2 ; but whether or not the addition of water to KOC_6H_5 causes double decomposition is not known from the diagram as far as investigated. Mixtures of phenol and KOH however, in any proportion, do undergo double decomposition. If KOH is added to solid phenol, the solid KOH is consumed in the reaction $HOC_6H_5 + KOH \rightarrow HOH$ (in liquid b) + KOC_6H_5 (in compound D_1). When the total composition reaches the line bD_1 , the phenol has been consumed, leaving a liquid saturated with D_1 alone. With further addition of KOH the composition of the liquid moves on the curve byc , reaching c when the total composition reaches the line cD_1 . At this point solid D_2 , or $KOC_6H_5 \cdot 2H_2O$, begins to precipitate, and all the liquid, with fixed composition c , will have been consumed when the total composition reaches the line D_1D_2 . Further addition of KOH may now cause appearance of solid KOC_6H_5 at the expense of D_1 , or it may simply leave solid KOH in excess; this section of the isotherm is unknown.

It should be clear, in conclusion, that all the ternary relations discussed in Chapters X–XIV may be applied to the reciprocal systems of this chapter. When the condensed “reciprocal system,” however, contains a quasi-binary diagonal, as is the case, for example, in the system $K_2Cl_2-MgSO_4$ of Fig. 15–24 and in the system $K_2Cl_2-CaF_2$,¹⁰ there is no necessity whatever, strictly, for treating it as reciprocal.

¹⁰ I. E. Krause and A. G. Bergmann, *Compt. rend. acad. sci. U.R.S.S.*, **35**, 20 (1942).

Chapter XVI Quaternary Systems

(Additive Type)

The simpler type of quaternary system is that involving no double decomposition, in which consequently all compositions may be expressed positively in terms of the four substances chosen as the components. This type then includes systems of four metals, four salts with a common ion, water and three salts with a common ion in absence of hydrolysis, two salts with a common ion + water + an organic solvent, etc.

A. Graphical Representation of the Isobaric Isotherm

1. The Tetrahedron

In a 4-component system, with three independent composition variables, graphical representation is usually limited to conditions of constant pressure

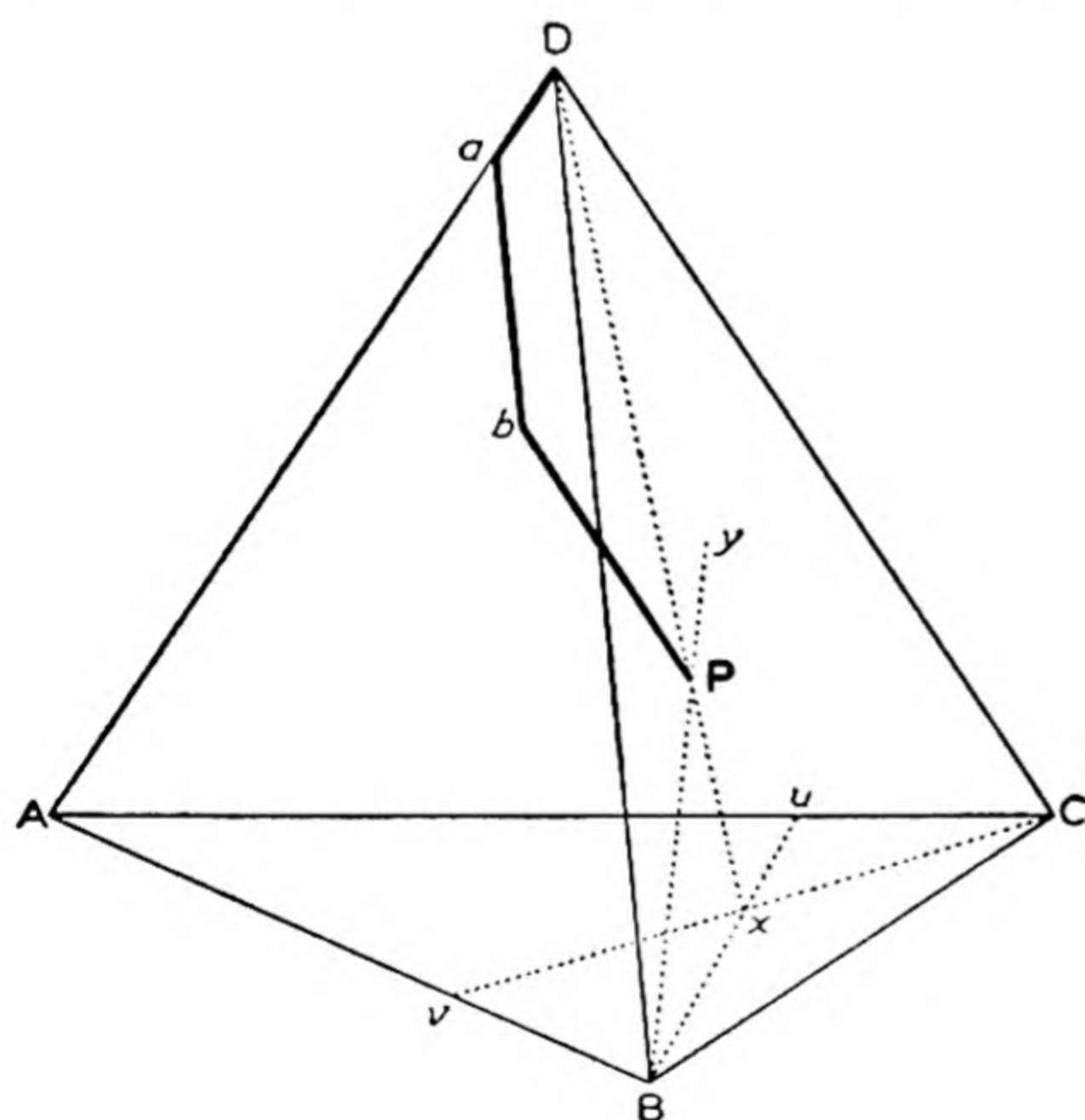


FIG. 16-1. Composition tetrahedron.

and temperature, since the composition itself requires a 3-dimensional space model for its representation. The isobaric isotherm for the additive quaternary system is therefore a 4-sided, 3-dimensional figure, each face of which is the isotherm of one of the four ternary systems making up the quaternary system.

For this purpose we may use a regular tetrahedron, so that each ternary isotherm will appear as usual as an equilateral triangle (Fig. 16-1). The corners represent the pure components, the edges binary mixtures, the faces the ternary systems, and

the interior quaternary compositions. The plotting of compositions in the tetrahedron is an extension of the principle of ternary plotting. The edge is taken as 100%. The percentage of each component for a point in the tetrahedron is taken as the distance from the point to the face opposite the component, measured parallel to any edge originating at that com-

ponent. The sum of the four parallels from any point to the faces of the tetrahedron equals the length of the side. To plot a point of known composition, P , the percentage of A ($=Da$) is measured along any edge, here DA , from the opposite face; from point a the percentage of B ($=ab$) is measured on the face ABD , parallel to DB toward B ; from b the percentage of C ($=bP$) is measured into the tetrahedron, parallel to DC . Now the parallel (not shown) from P to the base is the percentage of D . In Fig. 16-1, P represents the composition 10A, 20B, 30C, 40D.

The propositions given in Chapter X for the composition triangle may be extended for this regular tetrahedron. The ratio A/B is constant on any plane including the edge DC . The proportions of the three components A , B , and C are constant on any line through D . The composition of a mixture of two phases lies on the straight line joining the compositions of the phases, and the inverse ratio of the weights of the phases is that of the segments of the tie-line. Hence, with one more dimension to be considered, the calculation of phase ratios is essentially the same as in ternary isotherms.

A quaternary composition may be expressed not only in terms of three independent percentages (the fourth being the difference from 100) but also in terms of various proportions of individual components. The three independent variables, for example, may be taken as the two ratios A/B and A/C , together with $\%D$; point P now represents $A/B = \frac{1}{2}$, $A/C = \frac{1}{3}$, and $\%D = 40$. To plot P (Fig. 16-1), then, the proportion of A in $A + C$ is measured on the edge AC , at point u ; the proportion of A in $A + B$ is located at v on AB . From the intersection x , of uB and vC , the line xD is drawn, and P is placed on xD at a vertical height equal to 40% of the altitude of the tetrahedron, or so that $xP = 40\%$ of xD . The three independent variables may also be taken as the percentage of A and the percentage of B in $A + B + C$, together with $\%D$ in the total of the four components. Now the proportions of A , B , and C (16.7% A , 33.3% B , 50% C) are plotted in the usual way on the face ABC , to give point x of Fig. 16-1, and then P is again placed on xD , at 40% of xD . One may even tabulate the compositions in terms of the proportions of A , B , and C (two independent percentages, such as $\%A$ and $\%B$ in $A + B + C$) and the proportions of A , D , and C (involving one additional independent percentage, that of D in $A + D + C$). The proportions of A , D , and C (12.5% A , 37.5% C , 50% D) fix the point y on the face ADC (Fig. 16-1) and the intersection of yB with xD fixes P .

It is clear that the compositions may be tabulated and expressed in various units (all numerically interchangeable) and that the procedure of plotting may be varied accordingly, but the resulting point in the tetrahedron is identical, and the 3-dimensional phase diagram is always the same.

The ternary diagrams on the faces of the tetrahedron involve curves of 2-phase equilibria (such as solubility curves for liquid + 1 solid, or for two conjugate liquids) and isothermally invariant points of 3-phase equilibria (such as liquid + 2 solids). Each such curve is the ternary edge of a quaternary surface of the same 2-phase equilibrium, and each such point is the origin of a quaternary curve of the same 3-phase equilibrium. The quaternary solubility surfaces (saturation with respect to one solid, for example) intersect along these curves; and three such curves meet at a 4-phase point, isobarically and isothermally invariant.

2. Projections of the Tetrahedral Diagram

By means of a suitable pair of plane projections of the tetrahedral diagram it is possible to represent graphically and without a solid model, the curves and points of intersection of the (isobaric, isothermal) bivariant surfaces of the system, that is, the intersections of solubility surfaces or of miscibility gaps, etc. The two projections may be of the same type but on different faces of the tetrahedron, and sometimes even projections from two

points of view upon the same face. Five types of projection will be described.

a. *Triangular orthogonal*: an orthogonal, or orthographic, projection, perpendicular to a face. In such a projection upon the face ABC, for example, the point D appears as the center of the composition triangle ABC. All four ternary systems are completely and explicitly represented, the system A-B-C by the full equilateral triangle ABC itself, and the other three by isosceles triangles, in which the D scale differs from that for the other components. But any point, whether binary, ternary, or quaternary, may be plotted as follows: the percentage of each of the components A, B, and C is augmented by one third of the percentage of D, and then plotted in the usual way on the composition triangle ABC. Thus the composition 10A, 20B, 30C, 40D is represented as P_1 in the lower part of Fig. 16-2, as

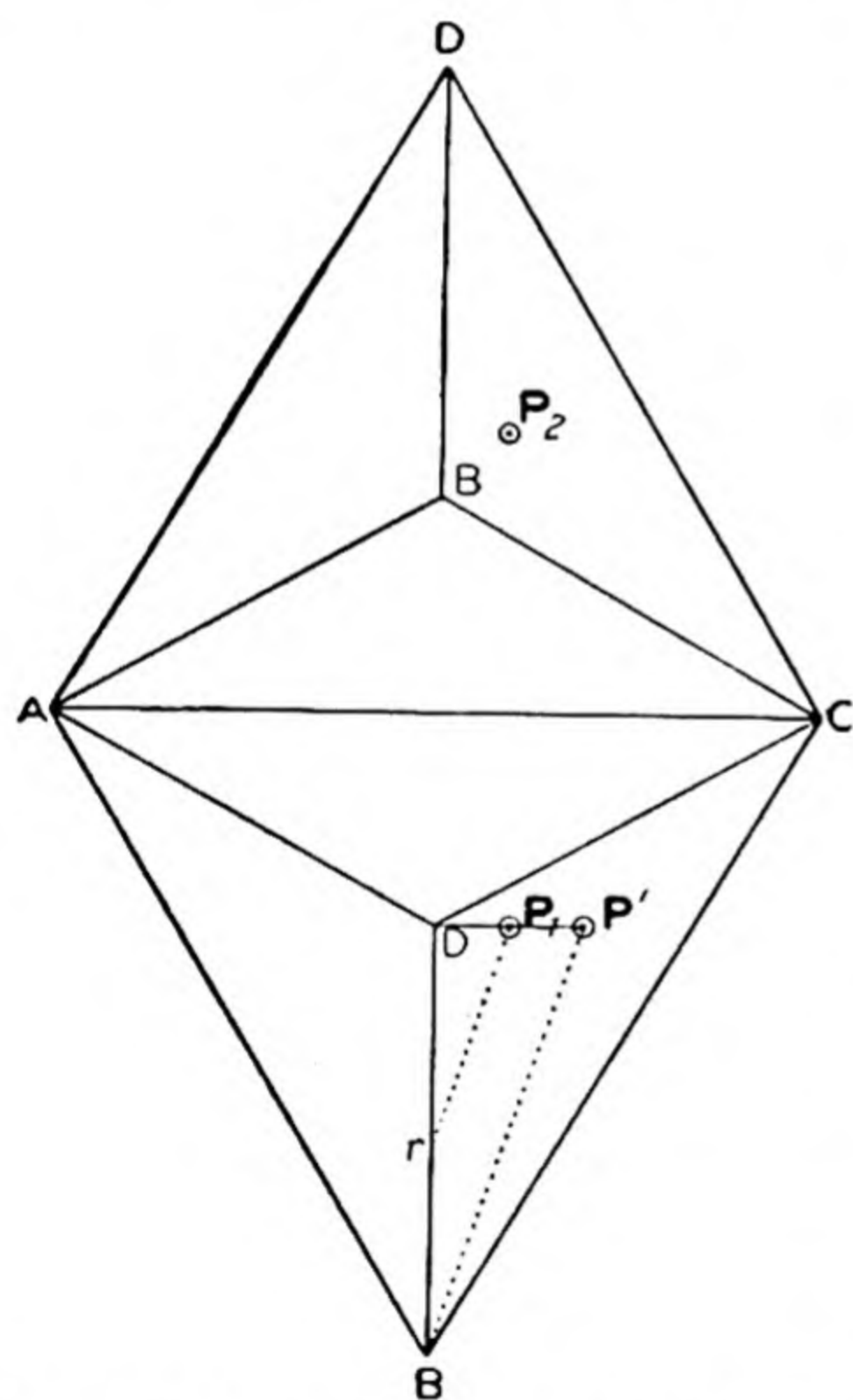


FIG. 16-2. Triangular orthogonal projections.

23.3A₁, 33.3B₁, 43.3C₁. But from the plotted point P_1 the composition cannot be read without further information such as a table giving %D at any point (approximated sometimes by means of contour lines of fixed D content), or a second projection, which may also be an orthogonal one on a

second face such as ADC, the upper part of Fig. 16-2. In this projection each of the three percentages plotted is first augmented by one third of the percentage of B, so that the same quaternary point here appears as P_2 , plotted as $16.7A_2$, $36.7C_2$, $46.7D_2$. To read the composition from the pair of points, we may proceed by finding $\%D$ as $(\frac{9}{8})(D_2 - B_1/3) = (\frac{9}{8})(46.7 - 33.3/3) = 40$. With $\frac{40}{3}$ subtracted from each of the values A_1 , B_1 , C_1 , we have $10A$, $20B$, $30C$, $40D$, or P .

b. *Square orthogonal*: an orthogonal projection on a plane drawn parallel to two edges of the tetrahedron which do not intersect one another.¹ The projection plane is now a square with two edges of the tetrahedron as its diagonals. In Fig. 16-3(a) the projection is upon a plane parallel to the

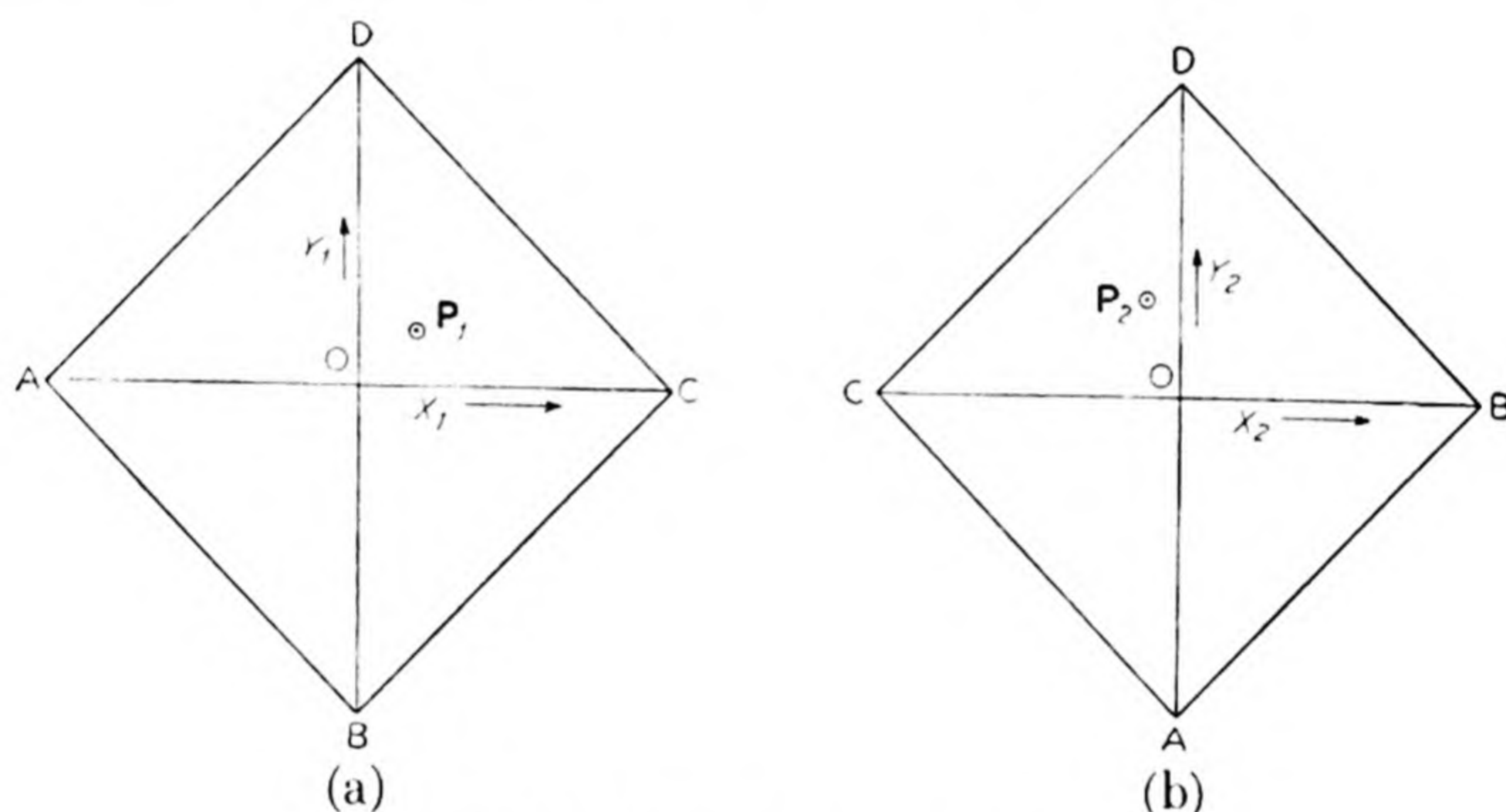


FIG. 16-3. Square orthogonal projections.

non-intersecting edges AC and BD. For the purpose of plotting the projection, these edges are taken as rectangular axes, with the intersection of their projections, O, as the origin. With AC as the X axis, and with the length AC still representing 100%, X is plotted as $(\%C - \%A)/2$, while $Y = (\%D - \%B)/2$. The point P therefore appears as P_1 in Fig. 16-3(a), with $X_1 = +10$, $Y_1 = +10$, and as P_2 in the square orthogonal projection of Fig. 16-3(b), with $X_2 = -5$ and $Y_2 = +15$. To read the composition from the pair of points we may proceed by finding $\%A$ as $(50 - X_1 + Y_1 - 2Y_2)/2 = (50 - 10 + 10 - 30)/2 = 10$, whereupon the other percentages follow immediately: C from X_1 and D from Y_2 .

c. *The Schreinemakers projection*, parallel to an edge.² This is the projection on a face, such as ABC, parallel to an edge from the opposite corner,

¹ F. A. H. Schreinemakers, *Z. phys. Chem.*, **65**, 553 (1909).

² F. A. H. Schreinemakers, *ibid.*, **59**, 642 (1907). Schreinemakers has used most of these projections, but this one is sometimes referred to particularly as the "Schreinemakers projection."

here D. This amounts to superimposing the point D with A, B, or C, if the projection is made parallel to the edge DA, DB or DC respectively. In the first case the resulting triangular diagram is either ABC or DBC, hence (A, D)BC; in the second it is A(B, D)C; and in the third AB(C, D). In the first case we plot %C from the corner (A, D) toward C and %B from the corner (A, D) toward B; hence the composition P under discussion now appears at P_1 in Fig. 16-4. Again the composition cannot be read from the

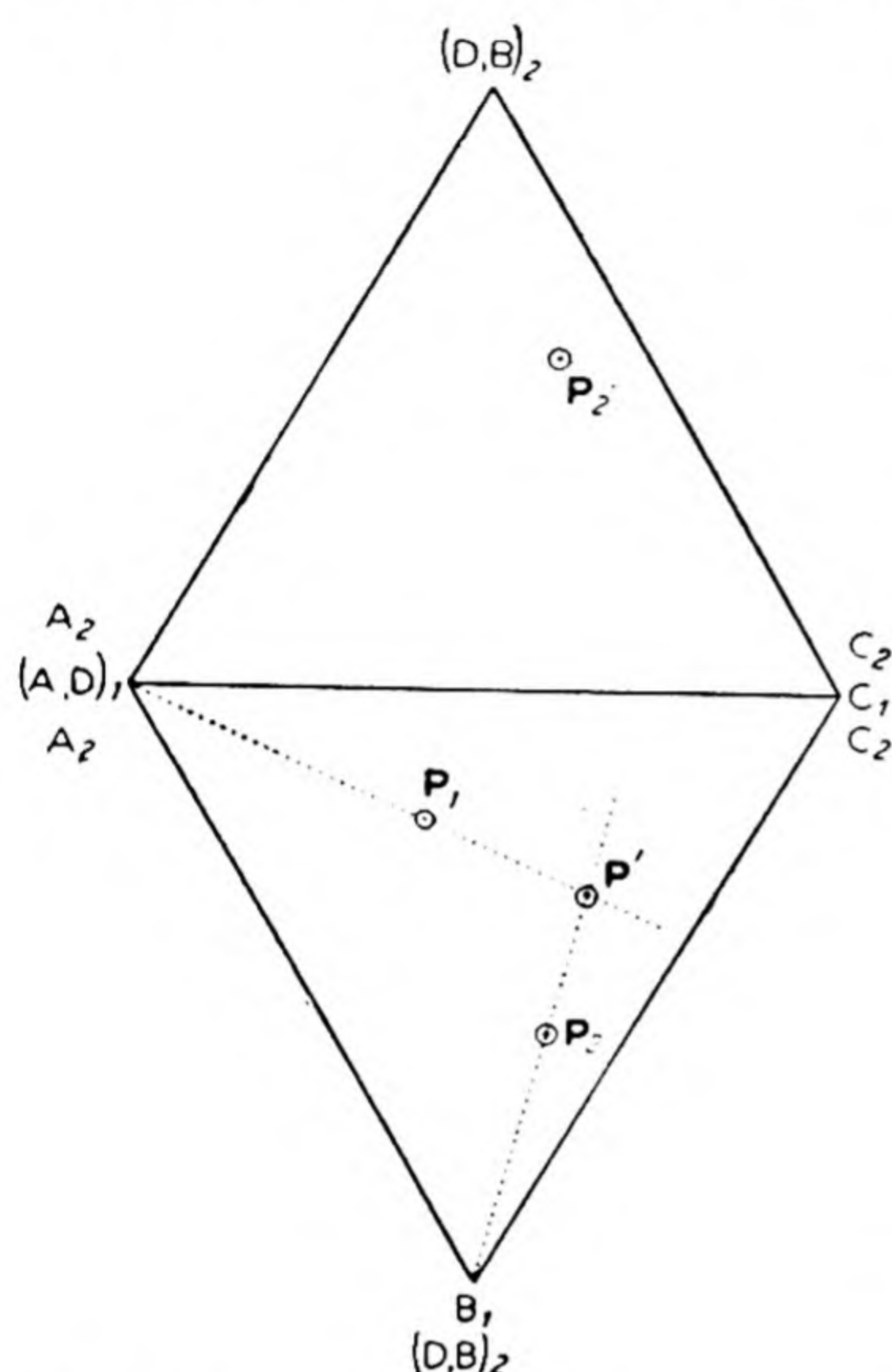


FIG. 16-4. Schreinemaker's projections.

plotted point without further information, which may be an accompanying table of the percentage of one of the other components or an accompanying second projection. The second projection may be a similar Schreinemaker's projection on a different face, or even one on the same face from a different point of view. Thus in Fig. 16-4 (upper part), %A and %C may be read from P_2 in the projection on $A_2(D, B)_2C_2$, and %B and %C from P_1 in the (lower) projection on $(A, D)_1B_1C_1$. In a sense these are two projections on the same face (ABC), one parallel to AD, the other parallel to BD, and they may even be superimposed, as in the lower part of Fig. 16-4. In such a diagram, the points and curves with subscript 1 give %B and %C, while those with subscript 2 give %A and %C; the two projections, P_1 and P_2 , fall, in other words, on a line parallel to the left side, which may be called the ABD side, and which is the projection actually of the ABD face of the tetrahedron.

d. *The semiperspective projection.* By this we shall mean a projection on a face, such as ADC, viewed parallel to the face ABC and perspectively from the edge DB. The result is a diagram showing the ratio A/C and %D. The proportion of A in $A + C$ is plotted at point u (Fig. 16-5), and then P_1 is placed on uD so that $100 (uP_1/uD) = \%D$. The actual triangle used need not be equilateral, since the units of the two independent scales are different; an isosceles is sufficiently convenient. Again the interpretation of the plotted point requires further information, such as a tabulation of the ratio A/B, C/B, etc., or a second projection. In Fig. 16-5 this is taken as a second semiperspective projection (which must now be on a different face in order to introduce the B content), on the face BDA, parallel to ABC and per-

spectively from the edge CD. In this figure, therefore, the right-hand projection P_1 gives %D and the ratio A/C, while the left-hand one P_2 supplies the ratio B/A, whereby the total composition is determined.

e. *The Jänecke projection*,³ in which the diagram is projected radially or in complete perspective, from a corner to the opposite face. The Jänecke projection on the face ABC therefore shows only the proportions of the three

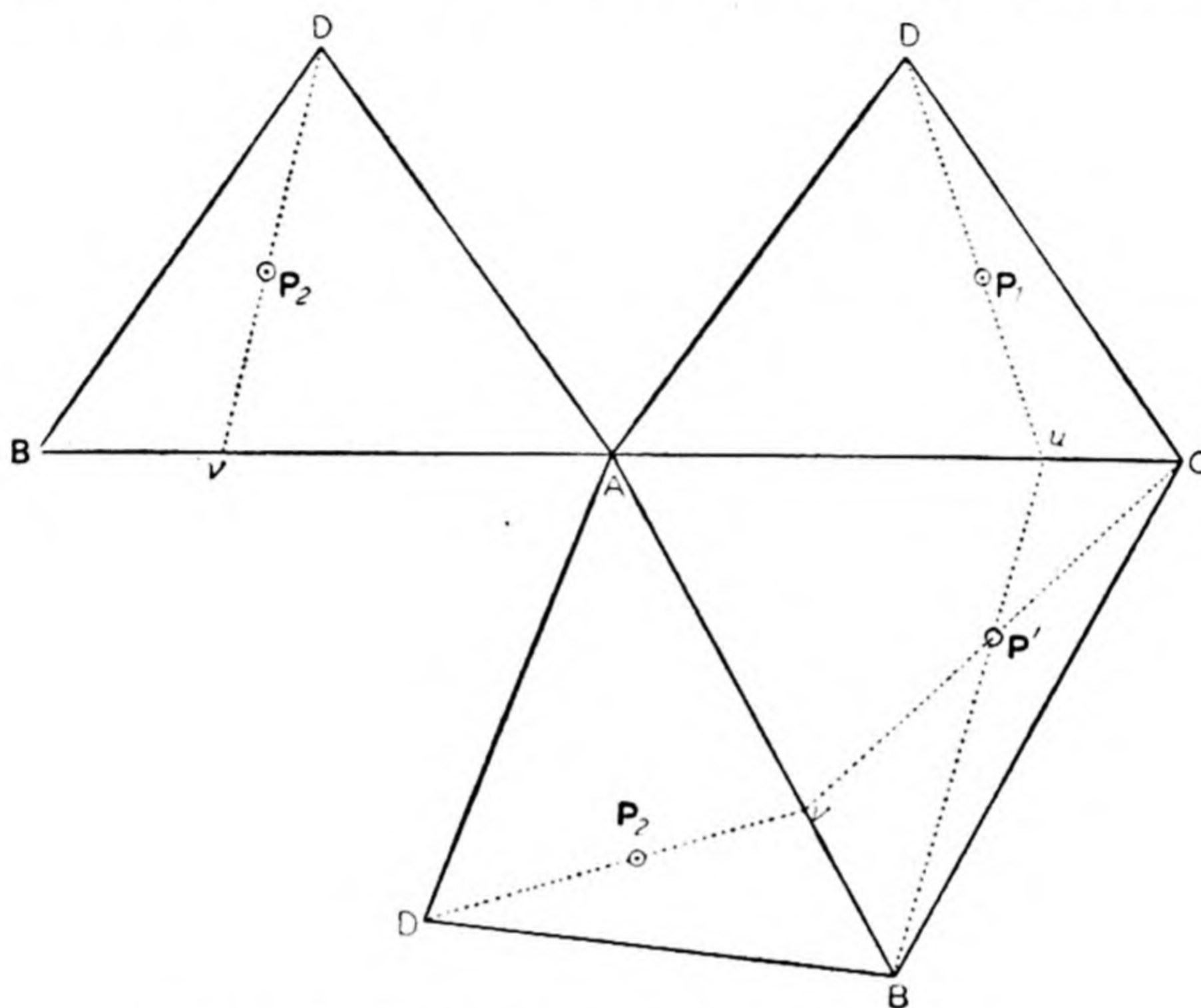


FIG. 16-5. Semiperspective projections.

components A, B, and C among themselves. Now the D content is tabulated separately, or shown approximately by contours of D content, for the interpretation of a plotted point. Alternatively, a pair of projections may be used, the second being one on a different face, or some different projection on the same face. With two Jänecke projections, for example, that on the face ABC gives the quantities of A, B, and C in 100 parts of these components, and that on ADC gives the ratio D/A or D/C, whereby the total composition is determined. In Fig. 16-1, x is the Jänecke projection of P on ABC, and y its Jänecke projection on ADC. If A' is the value of A plotted on ABC, or $100 \times \%A/(100 - \%D)$, and A_1 the value plotted on ACD, or $100 \times \%A/(100 - \%B)$, we have $\%D = 100 - 100A_1/(A' + B'A_1/100)$; then $\%A = A'(100 - \%D)/100$, $\%B = B'(100 - \%D)/100$, etc.

The number of projections of each type will be seen to be 4, 3, 6, 12, and 4, respectively. A suitable pair of these 29 projections suffices for the complete representation of a quaternary composition. Although a single pro-

³ E. Jänecke, *Zeit. anorg. Chem.*, **51**, 132 (1906); **52**, 358 (1907); **53**, 319 (1907). Also, H. LeChatelier, *Compt. rend.*, **172**, 345 (1921).

jection is insufficient for reading the composition of a plotted point, a pair may always be used for the purpose. If, for example, A' and A_1 are the values of A as plotted respectively for the Jänecke and for the orthogonal projections of a point on the same face, ABC , so that $A' = 100 \times \%A / (100 - \%D)$ and $A_1 = \%A + \%D/3$, then $\%D = 100(A' - A_1) / (A' - 100/3)$, whereupon the other percentages follow directly from the orthogonal coordinates. If A' refers to the Jänecke projection on ABC and A_1 to the orthogonal on ACD , so that $A_1 = \%A + \%B/3$, then $\%D = 100 - 100A_1 / (A' + B'/3)$, $\%A = A'(100 - \%D) / 100$, etc.

3. Graphical Interrelations of the Projections

For certain quantitative considerations it is sometimes desirable to transform a given projection graphically into one of another type, on the same or on a different face. For this purpose it is necessary to know the complete quaternary composition, so that we must start either with a pair of projections or with a single projection accompanied with a table supplying the missing composition quantity. As will be seen later, the transformation most likely to be required is that into a Jänecke projection. Fig. 16-4, lower part, illustrates the transformation of a pair of Schreinemakers projections into a Jänecke projection on the same face. Here the intersection of the line $(A, D)_1P_1$, which fixes the proportion of B and C , with the line $(D, B)_2P_2$, which fixes the proportion of A and C , determines P' , the Jänecke projection on the face ABC . Similarly the lower part of Fig. 16-5 shows the transformation of semiperspective projections on the sides of the tetrahedron (P_1, P_2) into a Jänecke projection on the base ABC , or point P' . The lines DP_1 and DP_2 are extended to the bases at u and v respectively. P' follows as the intersection of Bu with Cv on the Jänecke triangle ABC .

In the lower part of Fig. 16-2 the triangular orthogonal projection P_1 is transformed to a Jänecke projection P' on the same face. With $\%D$ known either from a table or, as already explained, from a combination of projections, the line DP_1 is extended so that $100 P_1P' / DP' = \%D$. This construction is conveniently carried out by the method of parallels: measuring $\%D$ as Br , relative to BD as 100% , connecting r to P_1 , and then drawing a line through B parallel to rP_1 , to fix the point P' at its intersection with the extension of DP_1 . In this manner any point of the orthogonal diagram may be transformed to its corresponding Jänecke projection. The two corresponding points will lie on a straight line through D , always at distances such that $100 P_1P' / DP' = \%D$.

In Fig. 16-6 the Jänecke projection P' on the face $AB'C$ is obtained from the triangular orthogonal projection P_2 on the face ADC . In this case we must know the B content of the point. By the method of parallels, BP_2 is

extended to P'' such that $100 P_2P''/BP'' = \%B$. P'' is now the Jänecke projection of the point on the ADC face. We now extend DP'' to a on the edge AC and draw aB and aB' . We also extend DP_2 to d , its intersection with aB . From d we drop a line perpendicular to AC, and its intersection with aB' fixes P' , the Jänecke projection on $AB'C$. A somewhat similar construction is shown in Fig. 16-7 for the transformation from a square orthogonal projection on the square ABCD to the Jänecke projection on

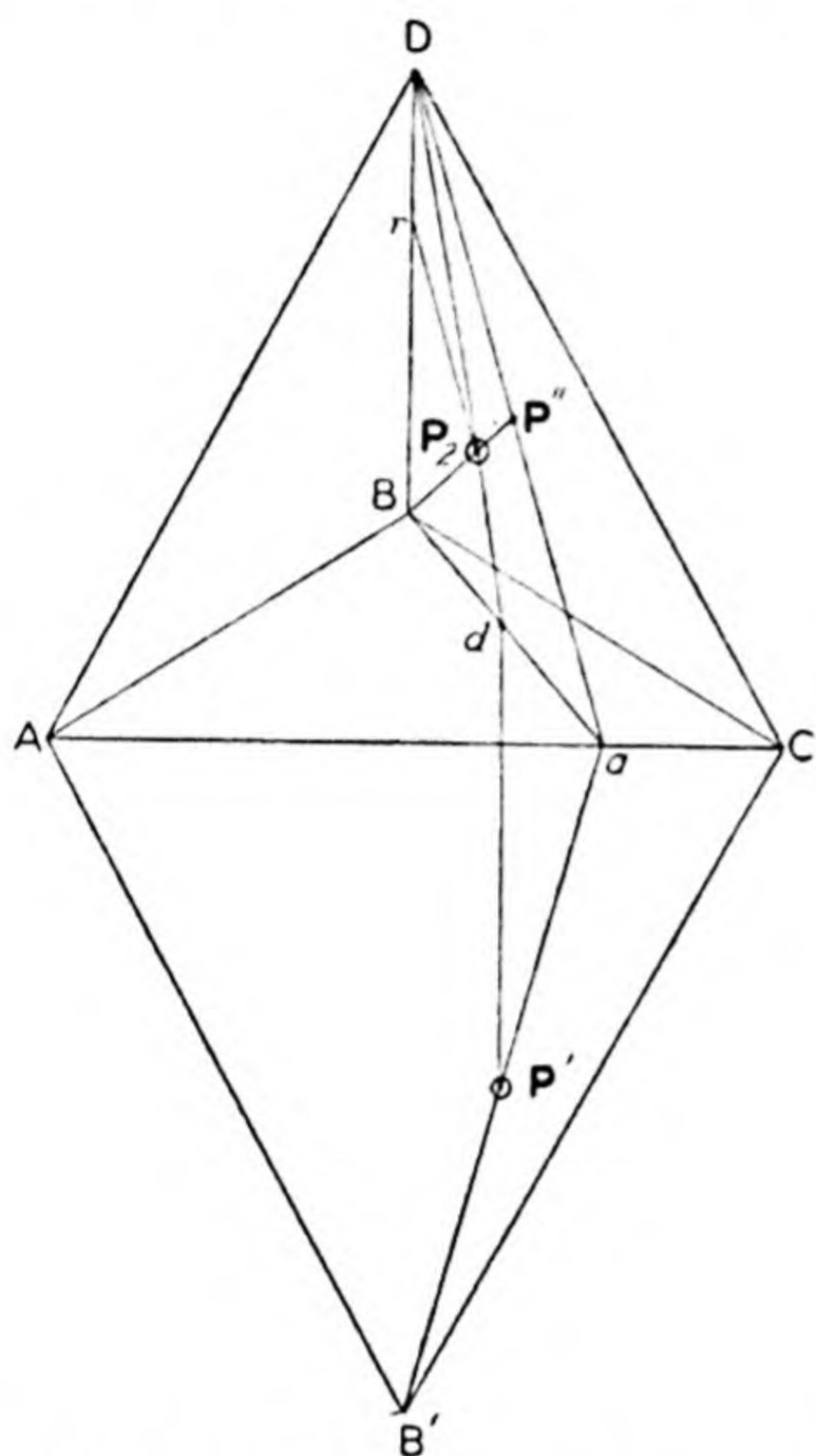


FIG. 16-6. Transformation between triangular orthogonal and Jänecke projections.

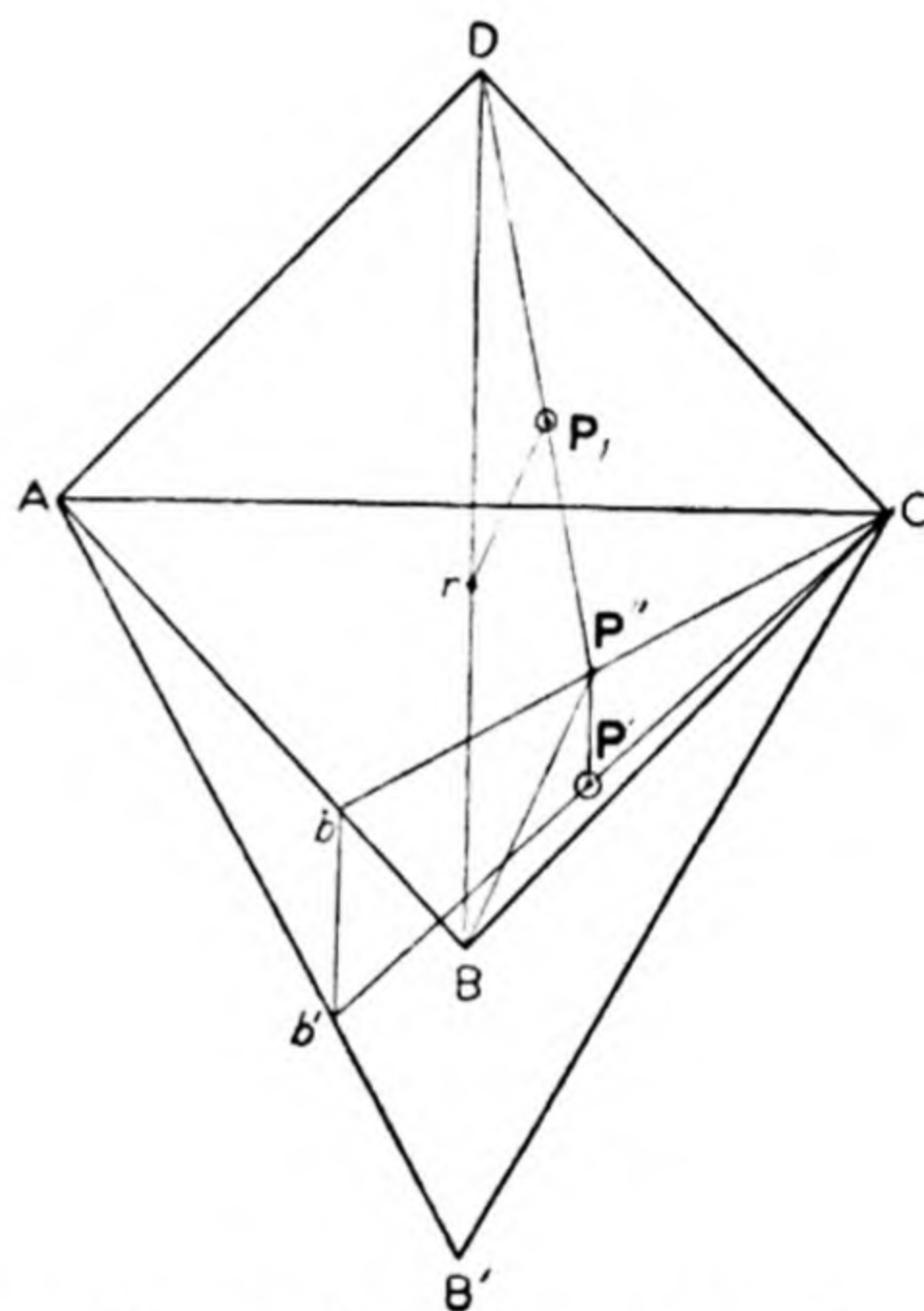


FIG. 16-7. Transformation between square orthogonal and Jänecke projections.

$AB'C$. In this construction we use the D content of P_1 , obtained either from a table or from two projections as explained under Fig. 16-3, and we extend DP_1 to P'' by the method of parallels (with $Br = \%D$) so that $100 P_1P''/DP'' = \%D$. P'' is now the Jänecke projection of the point on the ABC face, but the face is not on the plane of the paper. We extend CP'' to b on the edge AB, and drop a line from b perpendicular to AC, to the edge AB' , at point b' , and then draw $b'C$. Now a similar line from P'' , perpendicular to AC, fixes P' on $b'C$, P' being the required Jänecke point on $AB'C$.

It is clear in every case that the other projections may similarly be derived, in reverse, from the Jänecke on ABC, for example, if the D content is known.

Finally, the *tie-line* joining two phases in equilibrium, or in general the

line connecting any two compositions, appears as a straight line on any of these projections, and the total composition of the mixture of two phases falls on the straight line. But the usual relation between the ratio of the amounts of the two phases and the inverse ratio of the lengths of the segments of the tie-line holds only on the non-perspective projections, that is, on the two orthogonal and the Schreinemakers projections. Hence any suitable pair of projections may be used to plot the course of tie-lines in order to locate their common point of intersection, but only the non-perspective projections can give the phase ratios involved. The graphical solution of a particular problem in phase relations may therefore be done by means of a great variety of combinations of projections, but the combination used must include an appropriate non-perspective projection in order to make possible the graphical determination of the relative amounts of phases corresponding to the segments of a tie-line or to the divisions of a 3-phase plane triangle, etc.

4. Löwenherz Diagram ⁴

This is a method of representation often used when one of the four components, such as D, acts as the solvent for the other three (solid) components, A, B, and C. Now the quantities of each of the components A, B, and C, per fixed quantity of D, such as 1000 g or 100 moles, etc., are plotted on three axes intersecting as at the apex of a regular tetrahedron. This intersection point represents pure D, but the solid figure has no finite base, since the pure components A, B, and C lie at infinite distances from the origin upon their respective axes. The plotting of the quantities of A, B, and C per fixed amount of D is otherwise, however, the same as the plotting of the percentages of A, B, and C shown in Fig. 16-1. If the three axes are placed on one plane, intersecting at a common point (pure D) at equal angles, we have the coordinate system of Fig. 16-8. Now the composition **P** of the previous figures would be tabulated as containing 25 g of A, 50 of B and 75 of C per 100 g of D. It would be plotted as **P**₁, by measuring 25 units on the A axis from the origin D to the point *a*, 50 units from *a* toward B, parallel to the axis DB to the point *b*, and 75 units from *b* toward C, parallel to DC. The plotted point, however, cannot be read as a composition without a graphical construction making use of an accompanying table of the combined quantity of A + B + C (*N* units) per fixed quantity of D. In this case if it is known that **P** represents 150 units of A + B + C per 100 of D, we measure off the distance $Dr = 150$ units on one of the axes and the distance $rr' = 100$ units. A line through *r'*, parallel to rP_1 , fixes

⁴ R. Löwenherz, *Z. phys. Chem.*, **13**, 459 (1894).

the point P'_1 by intersection with the extension of DP_1 . We also complete the equilateral triangle $r'A'B'$ as $C'A'B'$. Now the proportions of A, B, and C are read from the position of P'_1 as a point in the composition triangle $A'B'C'$. The line DP_1 , therefore, is extended so that $P'_1P_1/DP_1 = 100/N$, and P'_1 is read in a triangle with side length $= \sqrt{3} (N + 100)$, in units of

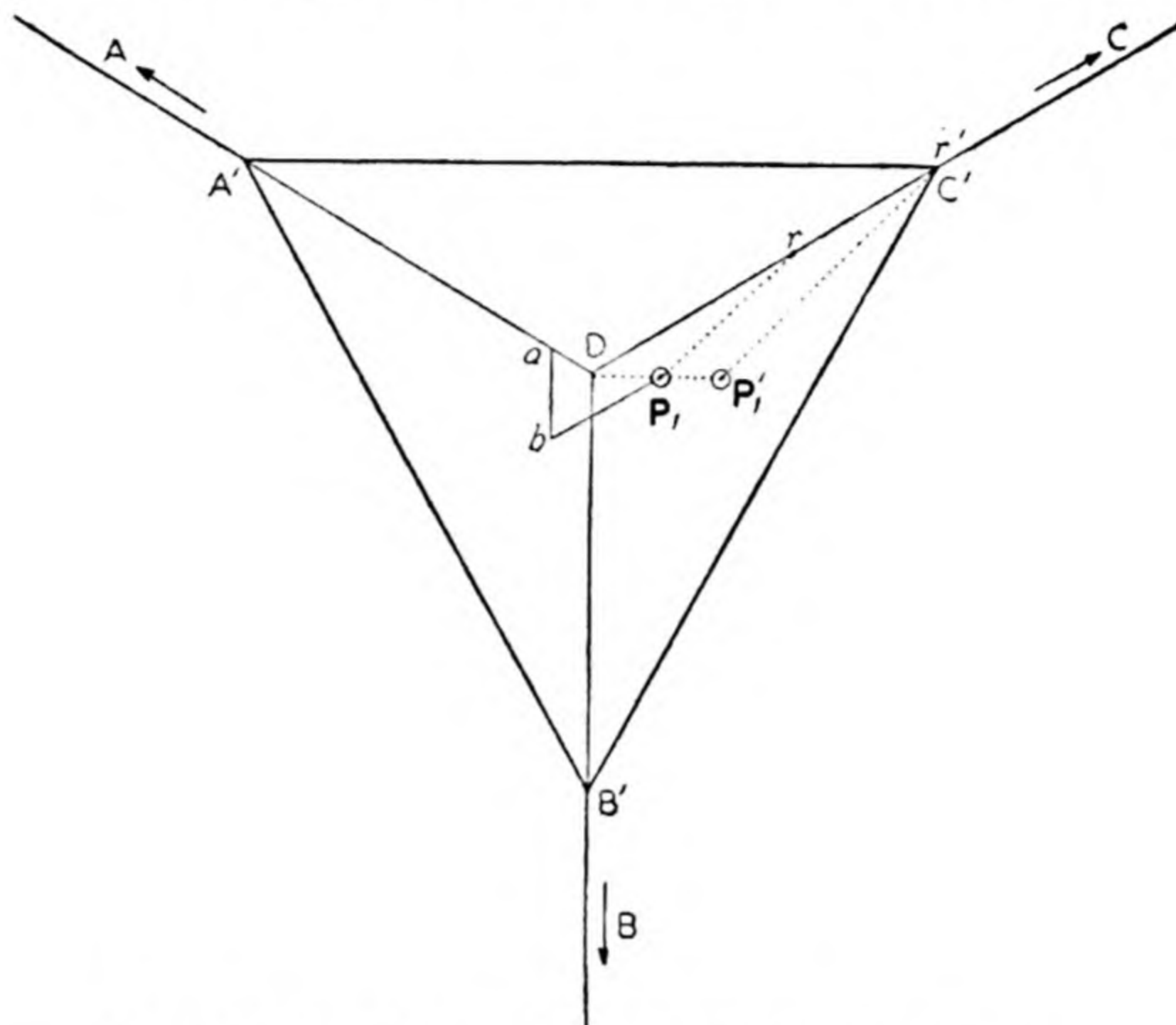


FIG. 16-8. Löwenherz method of plotting.

the scale of the Löwenherz axes. Since N varies from point to point in a Löwenherz diagram, a separate construction is required for reading the composition of each point, each requiring a composition triangle of particular dimension.

B. General Phase Diagrams (Condensed)

1. Isothermal Diagrams

Schematic representative isotherms for a (condensed) system involving four solid phases and in which no compounds are formed among the components are shown in Fig. 16-9, in the order of decreasing temperature. As T is lowered below the melting point of a component to give rise to a solid phase, there appears a solubility surface for that solid, representing the compositions of quaternary liquids saturated with respect to it. In Fig. 16-9(a) T has fallen below the melting points of both B and C so that there are two such surfaces which, however, do not touch each other until the eutectic of the binary system B-C is reached. The regions between these surfaces and the corners B and C represent 2-phase regions of liquid + solid B or solid C respectively. All the rest of the tetrahedron represents unsaturated liquid.

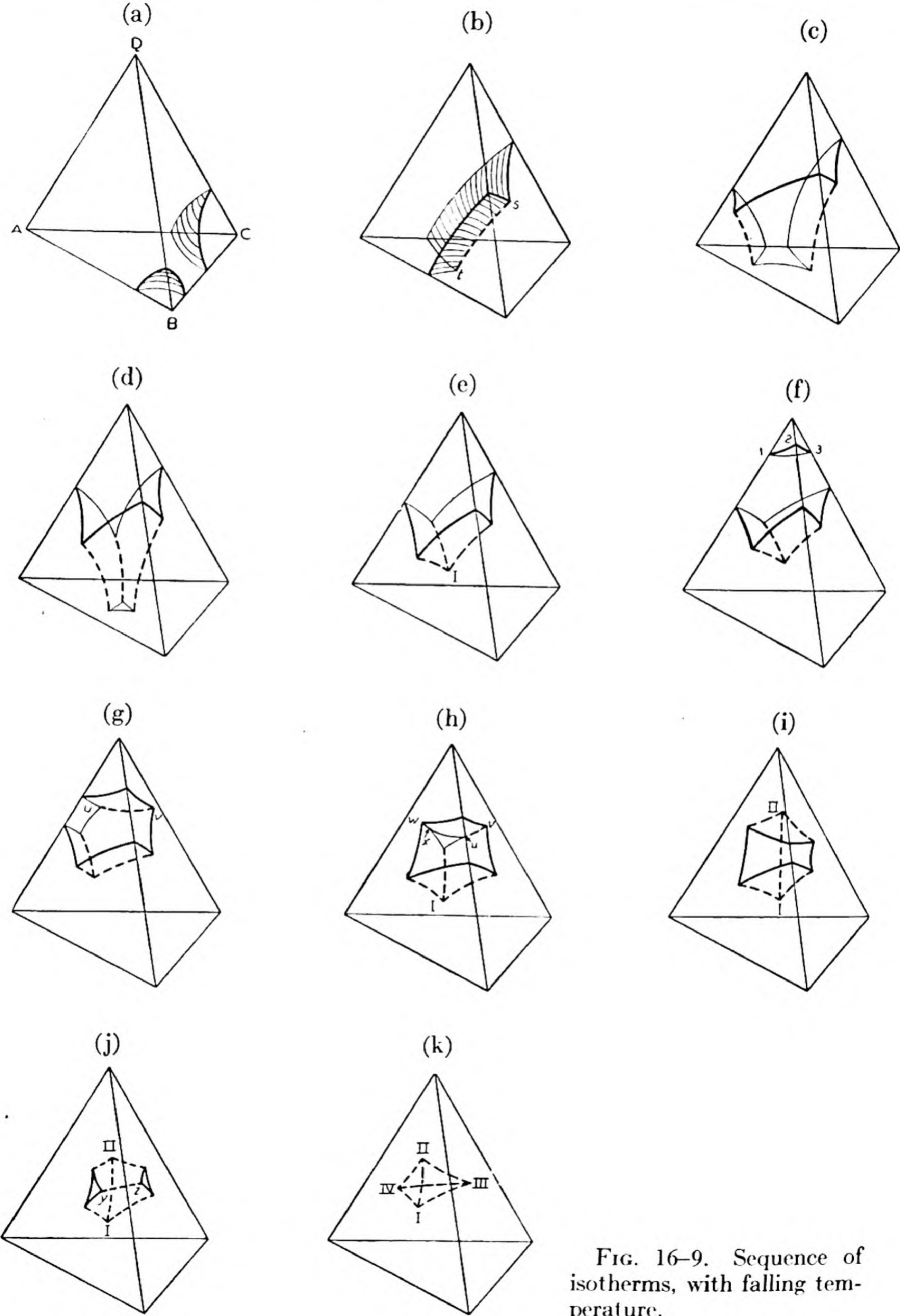


FIG. 16-9. Sequence of isotherms, with falling temperature.

In the following parts of Fig. 16-9 it is assumed that the temperatures of the (condensed) invariant points fall in the order BC (binary eutectic)-A (melting point of A)-AB-AC-ABC (ternary eutectic)-D-DC-DA-ADC-DB-BDC-ADB-ABCD (quaternary eutectic). In Fig. 16-9(b), therefore, with T between BC and A, the solubility surfaces of B and C have met, and their intersection, shown as broken curve st running from the DBC face to the ABC face, represents quaternary solutions saturated with both B and C. All quaternary curves of twofold saturation are shown in Fig. 16-9 as broken curves. Hence smooth curves represent the ternary boundaries of the surfaces, lying therefore on the faces of the tetrahedron, and broken curves the intersections of these surfaces within the quaternary system. In Fig. 16-9(c), with T between AB and AC (binary eutectics), there are three solubility surfaces and two quaternary curves of twofold saturation, one for $A + B$, the other for $B + C$. In all these figures the spaces between the surfaces and the corners and edges of the tetrahedron representing solid phases are heterogeneous mixtures of liquid + 1, 2 or 3 solid phases. The diminishing space, which in Fig. 16-9(c) is still open to the corner D, outside the solubility surfaces, is homogeneous unsaturated liquid. Fig. 16-9(d) is between AC and the ternary eutectic ABC. Hence there is still a region of ternary liquid on the face ABC, which region, however, disappears in the next isotherm, which is below ABC but still above the melting point of D. In Fig. 16-9(e), therefore, the three quaternary curves of twofold saturation meet at a quaternary isothermally invariant point I, representing liquid saturated with the three solids A, B, and C. Between the isotherms (e) and (f), T has fallen below the melting point of D, causing the appearance of the fourth solubility surface, labeled 1-2-3, that of D. Fig. 16-9(g) is below the binary eutectic DC, so that a fourth curve of twofold saturation has been introduced, for saturation with D and C, running from u on the ADC face to v on the BDC face. Between (g) and (h), T falls below the AD eutectic, and a fifth curve of twofold saturation appears, for $L + A + D$, running from w on the face ADB to x on ADC. The ternary eutectic ADC occurs between (h) and (i), so that a second isothermally invariant point, II, appears for the equilibrium $L + A + D + C$. Now the space for homogeneous, unsaturated liquid touches only two faces of the tetrahedron, ADB and BDC, but it is still open on the DB edge. The binary eutectic DB occurs between (i) and (j), and now the liquid region occupies, in (j), a tunnel-like space from the face ADB to BDC, and the sixth and last curve of twofold saturation has appeared, for $L + D + B$, running from y on ADB to z on BDC. As the two remaining ternary eutectics, BDC and ADB, are passed, between (j) and (k), the ternary liquids disappear, to give rise to two more points of threefold saturation, III for

$L + B + D + C$ and IV for $L + A + B + D$. In Fig. 16-9(k), therefore, which is below all the ternary eutectics but still above the quaternary eutectic, the liquid space is entirely inside the tetrahedron, not touching any of its sides, since it is limited to quaternary compositions. It is a four-sided space, its sides being solubility surfaces of saturation with a single solid; these surfaces intersect at six curves of twofold saturation, joining the points I, II, III, and IV, of threefold saturation. As T falls further this liquid space shrinks, preserving its general configuration, until all four points meet at the quaternary eutectic for the equilibrium $L + A + B + C + D$, a condensed or isobaric invariant point. Below this temperature the system consists at equilibrium of a mechanical mixture of the four solids.

2. Polythermal Projection

A representation of the freezing point relations of a quaternary alloy is possible,⁵ based upon the use of the polythermal projection of Fig. 12-18

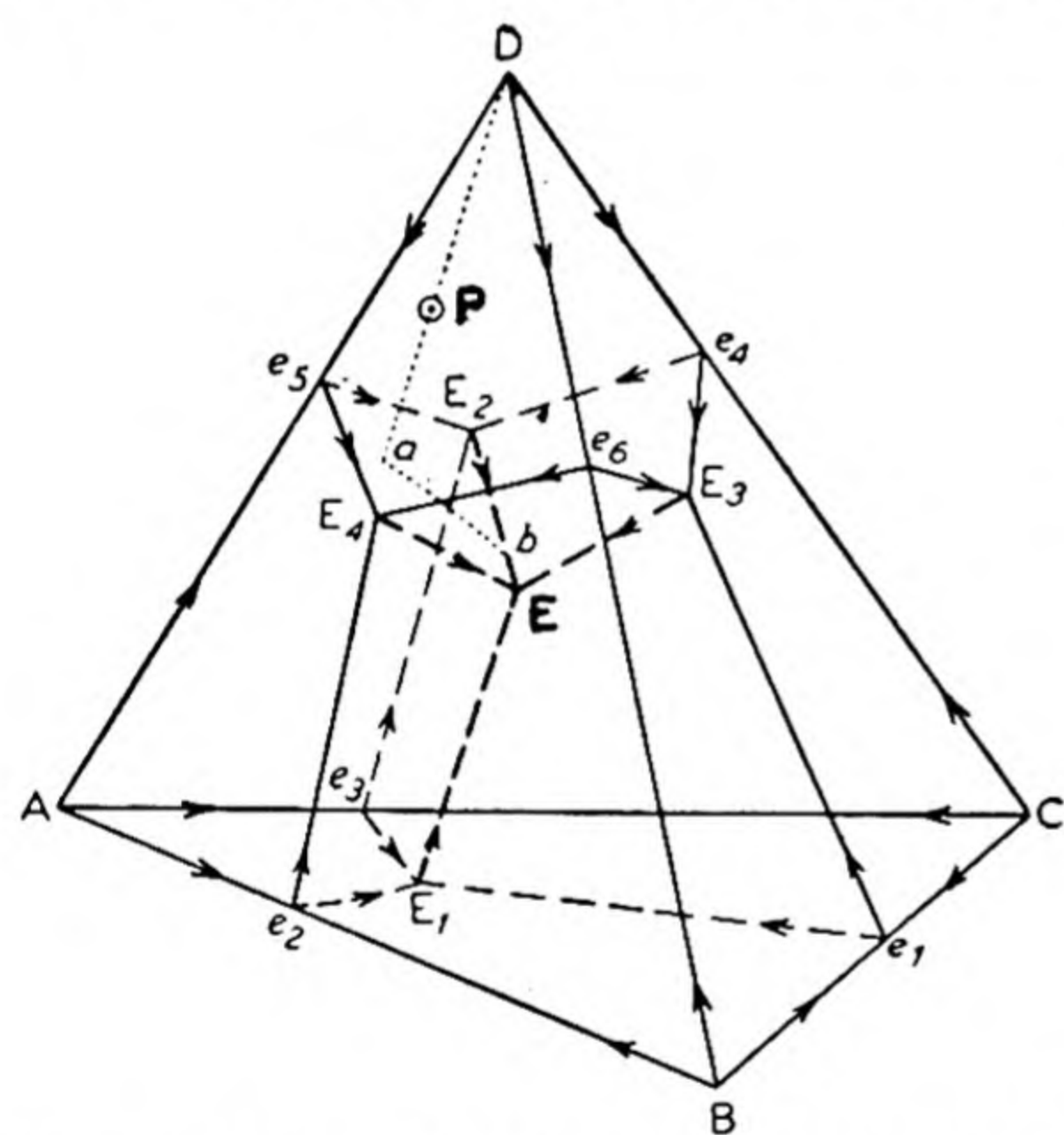


FIG. 16-10. Polythermal projection of Fig. 16-9.

on each ternary face of the tetrahedron, Fig. 16-10. The points e_1 to e_6 of Fig. 16-10 are the six binary eutectics (all relations have been assumed to be simple eutectic relations, as in Fig. 16-9, and the invariants have been numbered in the order in which they occur in that series of isotherms), and the direction of falling T is, of course, from the corners representing the pure components and their melting points, to these eutectics. Points E_1 to E_4 are the four ternary eutectics and E the quaternary eutectic. The curves e_1E_1 and e_1E_3 represent liquids crystallizing the pair $B + C$ in the two ternary systems ABC

and BCD respectively. Then the surface $e_1E_1EE_3$ represents quaternary liquids crystallizing the same pair on cooling. When three such surfaces meet, as on the curve E_3E , the curve represents liquids crystallizing three solids, here $B + C + D$, on cooling; and the four curves of threefold saturation meet at the quaternary eutectic E , where the liquid solidifies invariantly to the four solids,⁶ either isobarically or as a condensed system.

⁵ N. Parravano and G. Sirovich, *Gazz. chim. Ital.*, **41** (part 2), 697 (1911).

⁶ An example is the system $Pb-Cd-Bi-Sn$; N. Parravano and G. Sirovich, *ibid.*, **42**, 1 (1911).

In this figure, then, the surface $e_1E_1EE_3$ is generated by the curve st of Fig. 16-9(b). The curves E_1E and E_3E are generated by the points I and III respectively of Fig. 16-9.

If the liquid P of Fig. 16-10 is cooled, the point P will be reached, as T falls, by the crystallization surface of D ; cf. Fig. 16-9(f). The temperature then at which solid D first appears (first thermal break) cannot be read from Fig. 16-10, but from information contained in a number of successive isotherms such as Fig. 16-9. If the separating solid then is pure D , the composition of the liquid moves away from D on the line DP , until it meets the surface $e_5E_2EE_4$ at the point a . Sections and projections of the tetrahedron, after the fashion of those explained below for the graphical analysis of an isotherm, may be used for the determination of the composition of the liquid at this and at later points in the process of solidification; for such purpose the temperature must be related to the composition by means of tables or of contours on the surfaces of Fig. 16-10. At point a the liquid begins to precipitate D and A simultaneously, and its composition, with further cooling, proceeds on the surface of twofold saturation, following a curved path fixed by the intersection of the plane ADP with the surface, away from the edge AD , since A and D are being lost from the solution. The liquid then reaches the point b , on the curve E_2E , where C also begins to precipitate. With further cooling the liquid follows this curve, precipitating A , D and C , away from the face ADC , to the quaternary eutectic, where the residual liquid solidifies invariantly to a mixture of the four solids. Through methods explained below in connection with isothermal evaporation of aqueous salt systems, it is possible to calculate the relative amounts of the phases at any specified point in the process, and at any specified temperature, if the relation of the temperature to the composition in the tetrahedron is known, as by isothermal contours on the surfaces.

C. Aqueous System with Three Pure Salts as Solid Phases

1. Representation

a. *The isothermal tetrahedron.* This section will be a detailed discussion of the schematic relations of the isotherm of Fig. 16-9(e). If D is a liquid (water, hereafter called W) and A , B , and C are solids (three salts with common ion) at the temperature of the isotherm, we have Fig. 16-11. The space between the three surfaces and W is unsaturated liquid. The points a , b , and c are the solubilities of the individual salts in pure W . The points d , e , and f are the isothermally invariant ternary solutions saturated with the pairs $A + B$, $B + C$, and $C + A$ respectively. The surfaces $adQf$, $beQd$, and $cfQe$ are the quaternary solubility surfaces of A , B , and C respec-

tively. The curves dQ , eQ , and fQ are the quaternary solutions saturated with the pairs $A + B$, etc., and Q is the solution saturated with all three salts. Point P represents an unsaturated solution.

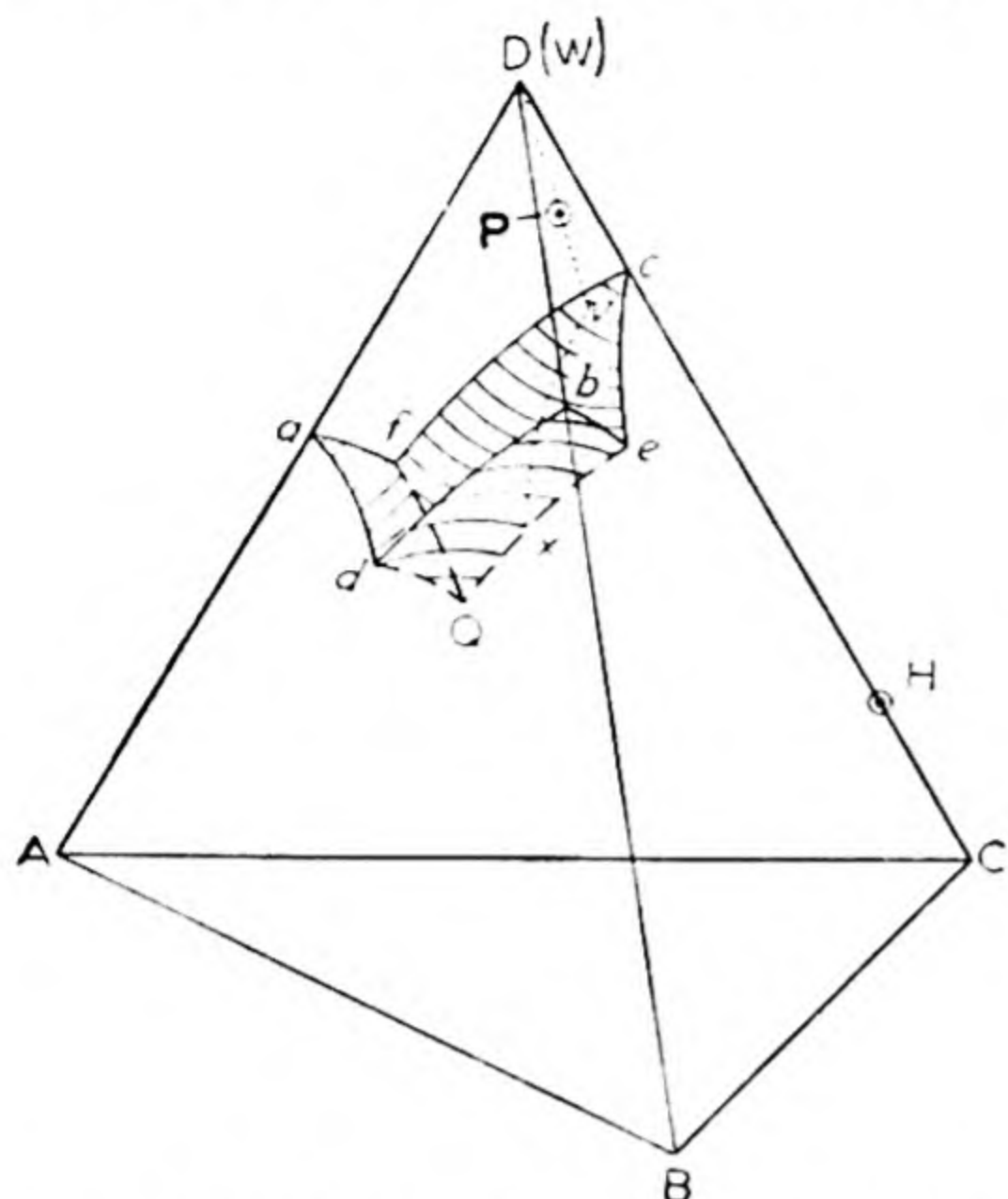


FIG. 16-11. Isotherm, water and three salts with common ion.

The C surface, or $cfQe$, is connected by tie-lines to the C corner; these tie-lines define a space of the form of Fig. 16-12(a). Any composition in this space consists, at equilibrium, of a liquid on the surface and solid C , the ratio of the phases being given in the usual way by the inverse segments of the tie-line. The curve eQ is connected by triangles to the edge BC , defining a space of the form of Fig. 16-12(b). A composition in this space consists at equilibrium of a liquid on the curve and a mixture of B and C ; the ratio of this mixture to the liquid is given by the segments of the line running from liquid to the edge BC through the total composition. Finally, the space between Q and the base (Fig. 16-12(c)) is an isothermally (condensed) invariant 4-phase system consisting of a mixture of liquid Q and the three salts. The relative proportions of the phases in this 4-phase space may be determined on the principle of center of gravity with respect to total composition. The segments of the line through Q and the total composition, and drawn to the base, give the ratio of Q to solid mixture, the composition

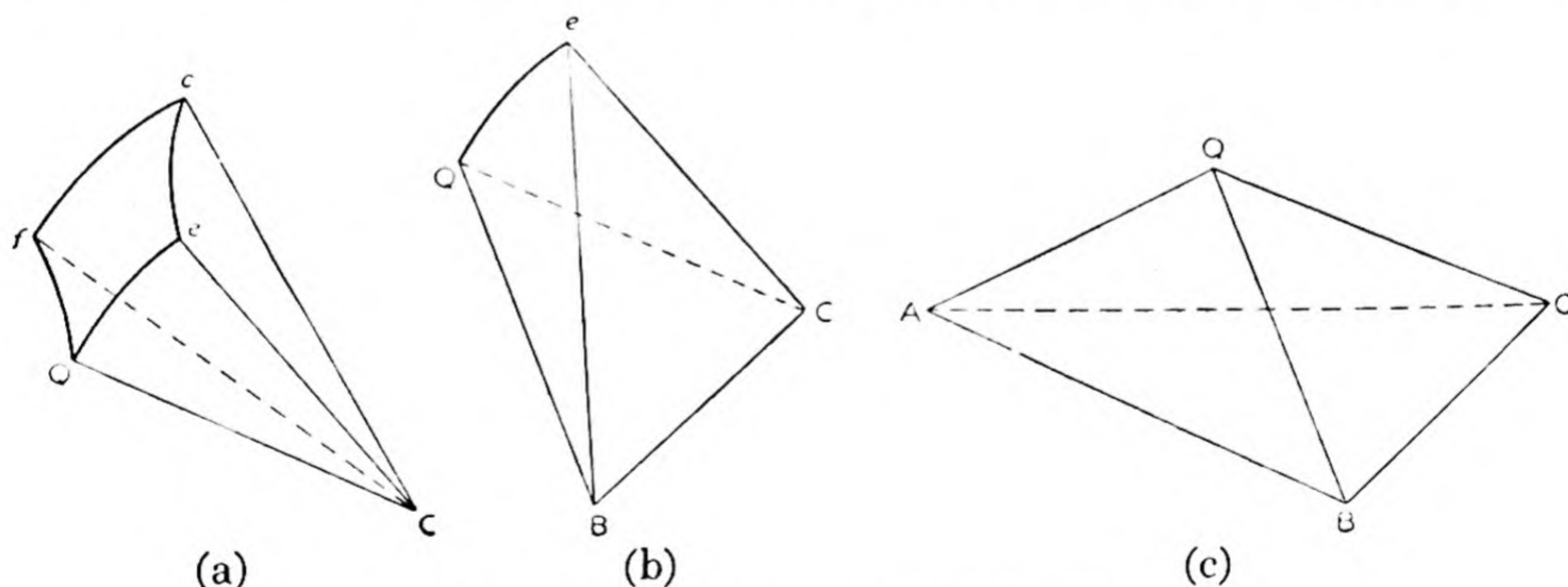


FIG. 16-12. Details of Fig. 16-11.

of which is then read in the usual way on the base. If C is a hydrated salt, with the composition H on Fig. 16-11, then the tie-lines in the space of Fig. 16-12(a) converge at H instead of C , the triangles of Fig. 16-12(b)

have BH as their common base, and the base of Fig. 16-12(c) is the plane ABH. The simple isotherm of Fig. 16-11 would be illustrated by the system $\text{NaHCO}_3\text{--Na}_2\text{SO}_4\text{--Na}_2\text{CO}_3\text{--H}_2\text{O}$ at 20° , in which, however, two of the solid phases are hydrated, namely, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.⁷

The points shown in Fig. 16-11 represent the hypothetical compositions of Table 16-1.

TABLE 16-1

Point	Weight Percentage				Grams per 100 g H ₂ O			
	A	B	C	W	A	B	C	N (total salts)
a.....	36	64	56.3	56.3
b.....	...	33	...	67	...	49.3	...	49.3
c.....	18	82	22.0	22.0
d.....	31	22	...	47	66.0	46.8	...	112.8
e.....	...	28	9	63	...	44.4	14.3	58.7
f.....	34	...	8	58	58.6	...	13.8	72.4
Q.....	30	21	5	44	68.2	47.7	11.4	127.3
P.....	4	10	6	80	5	12.5	7.5	25.0

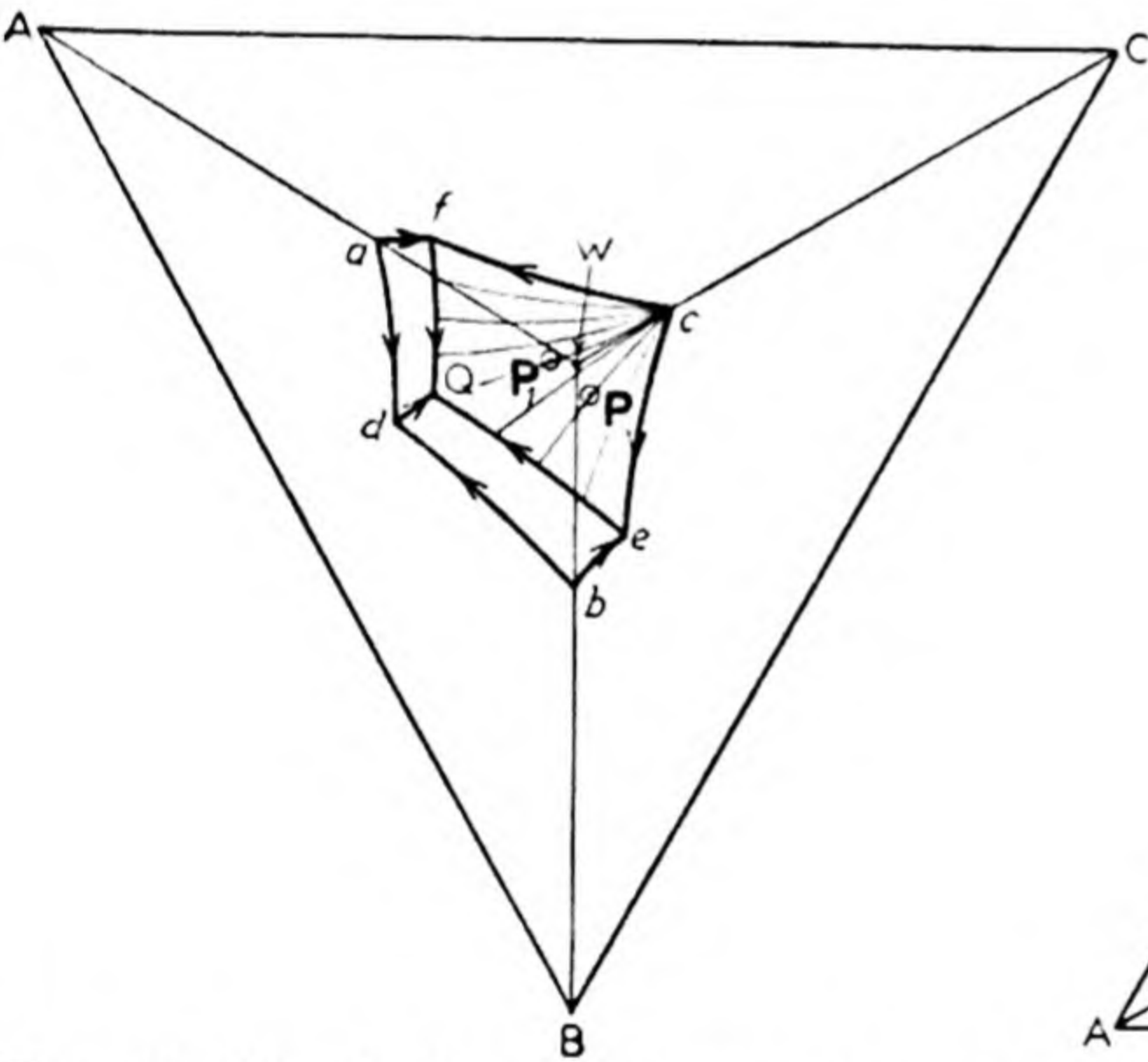


FIG. 16-13. Orthogonal projection of Fig. 16-11 on the base ABC.

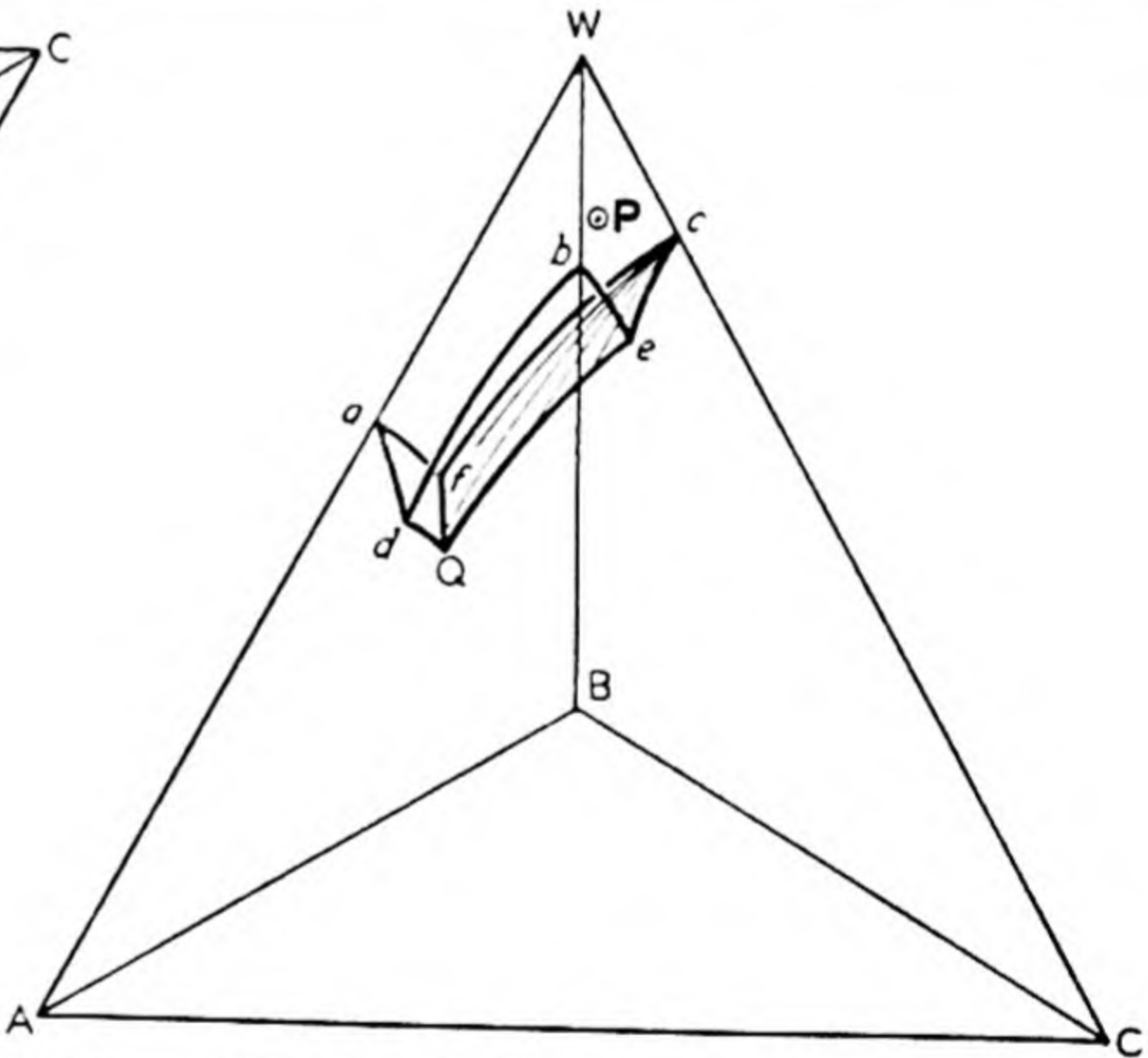


FIG. 16-14. Orthogonal projection of Fig. 16-11 on the face AWC.

b. *Projections and partial diagrams.* Some of the projections of the curves of Fig. 16-11 are shown in Figs. 16-13 to 16-18. Fig. 16-13 is the orthogonal projection on the base ABC, while Fig. 16-14 is also orthogonal, but on the face AWC. Fig. 16-15 is a square orthogonal projection, on an imaginary plane parallel to the edges AC and WB, which therefore appear

⁷ J. E. Teeple, *The Industrial Development of Searles Lake Brines*, Chem. Catalog Co., N. Y., 1929, pp. 156-157.

as the axes of the diagram, the diagonals of the square $AWCB$. Fig. 16-16 is a Schreinemakers projection upon the face $A(W, B)C$, parallel to the edge WB . Fig. 16-17 is a semiperspective projection on the face AWC , parallel to the base ABC and viewed perspectively from the edge WB . Fig. 16-18 is the Jänecke base projection, the radial or perspective projection upon the base ABC from the W apex.

In these projections the surfaces of Fig. 16-11 appear as areas or fields for saturation with respect to single salts. The C field is shown "shaded" in each figure, with lines which radiate from point c , the pure saturated solution of C , and which will later be discussed as crystallization paths for

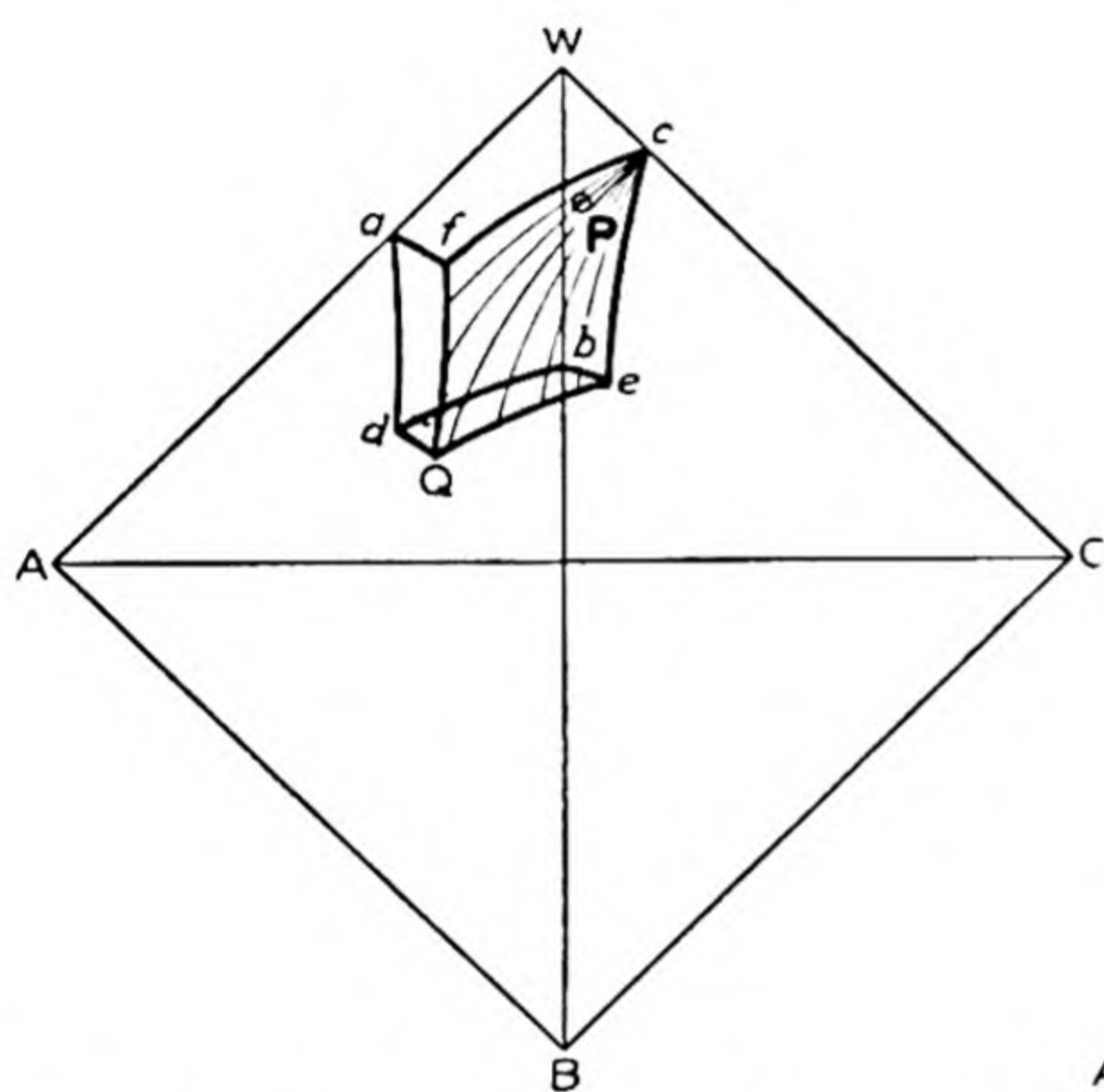


FIG. 16-15. A square orthogonal projection of Fig. 16-11.

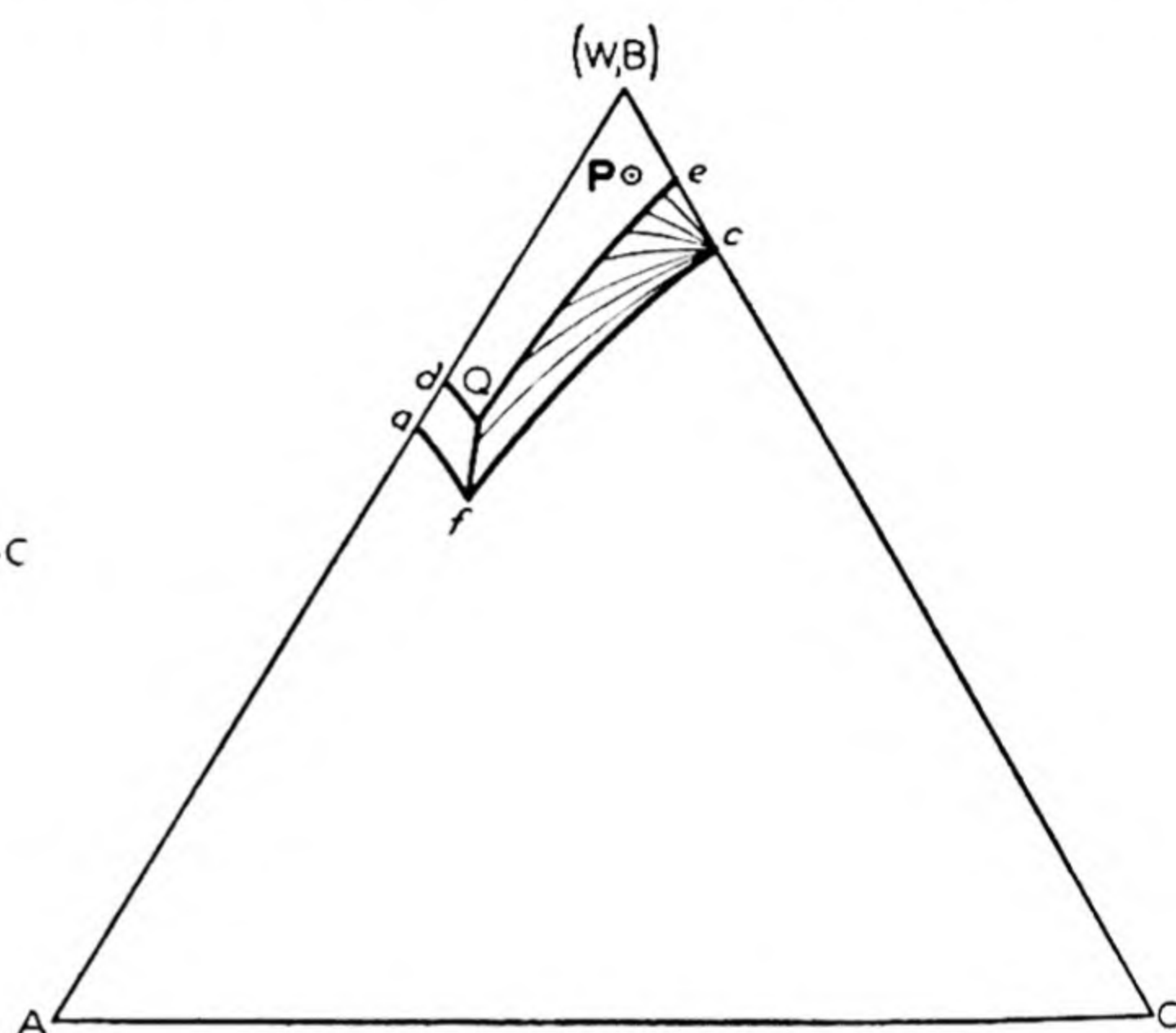


FIG. 16-16. A Schreinemakers projection of Fig. 16-11.

precipitation of C as sole solid phase in the process of isothermal evaporation. They are determined by the intersection of planes including the WC edge with the C surface, and they therefore appear as curves in all these diagrams except the Jänecke (Fig. 16-18), in which all such planes are projected as straight lines.

On the base projections, such as Figs. 16-13, 16, and 18, the concentration of the solvent D may be shown approximately by means of a certain number of contours of fixed D content, called isohydrores in the case of water as component D . Some isohydrores are shown in the C field of Fig. 16-18, as curves (continuous but not necessarily circular or regular) concentric at point C (or c). The water content normally, but not necessarily, falls from C toward points e and f , and along curves eQ and fQ toward point Q . Strictly, it is the water activity, or the vapor pressure, which thus falls. Point Q is therefore the point of minimum vapor pressure of all equilibrium

solutions of the isotherm, and it is usually also the point of minimum water content, at least in molar units of concentration. But complexities of non-ideality may cause the analytical water content of a ternary invariant point

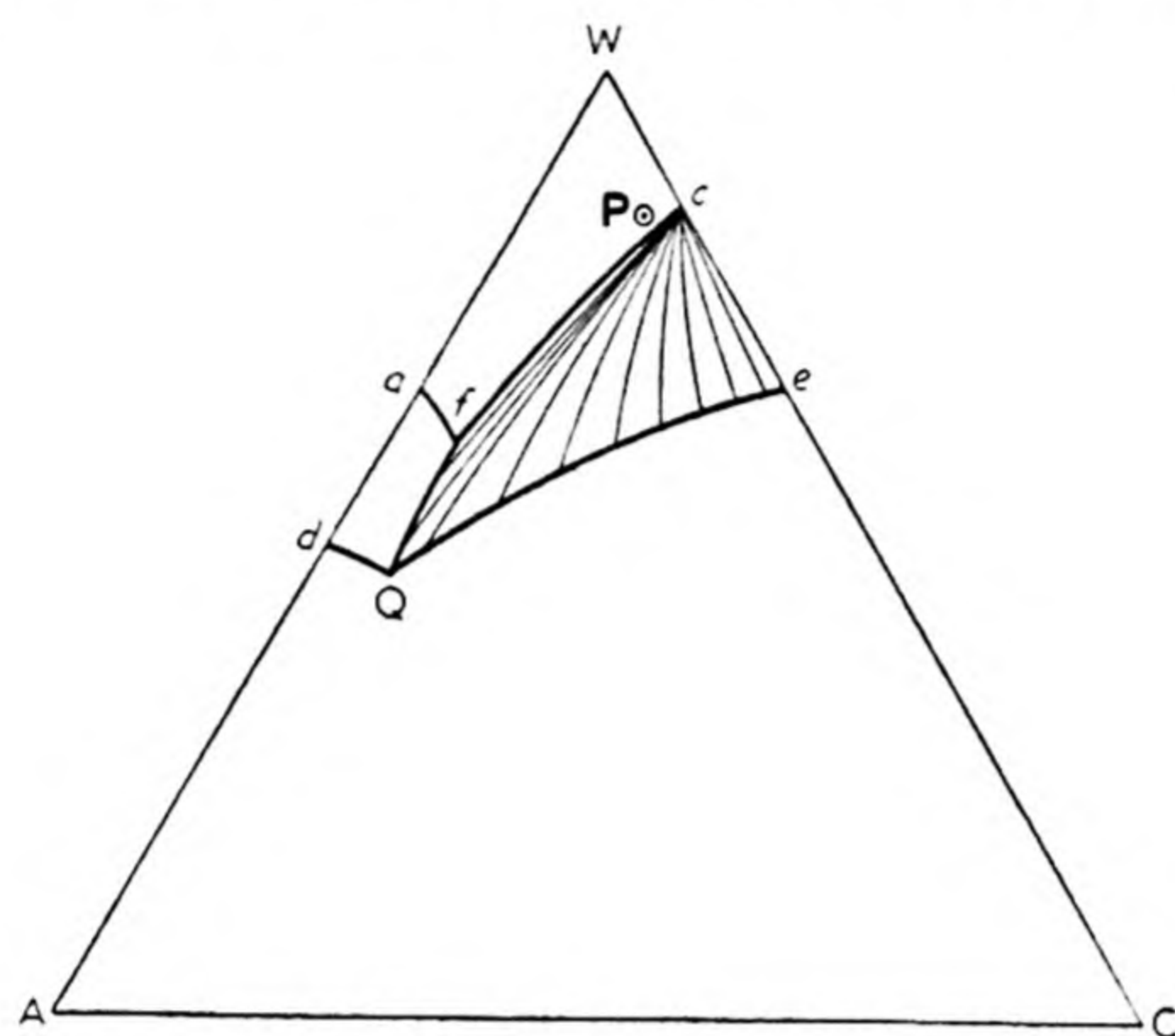


FIG. 16-17. A semiperspective projection of Fig. 16-11.

such as f to be higher than that at C , and may similarly cause the quaternary minimum of the analytical water content to occur somewhere other than at Q .

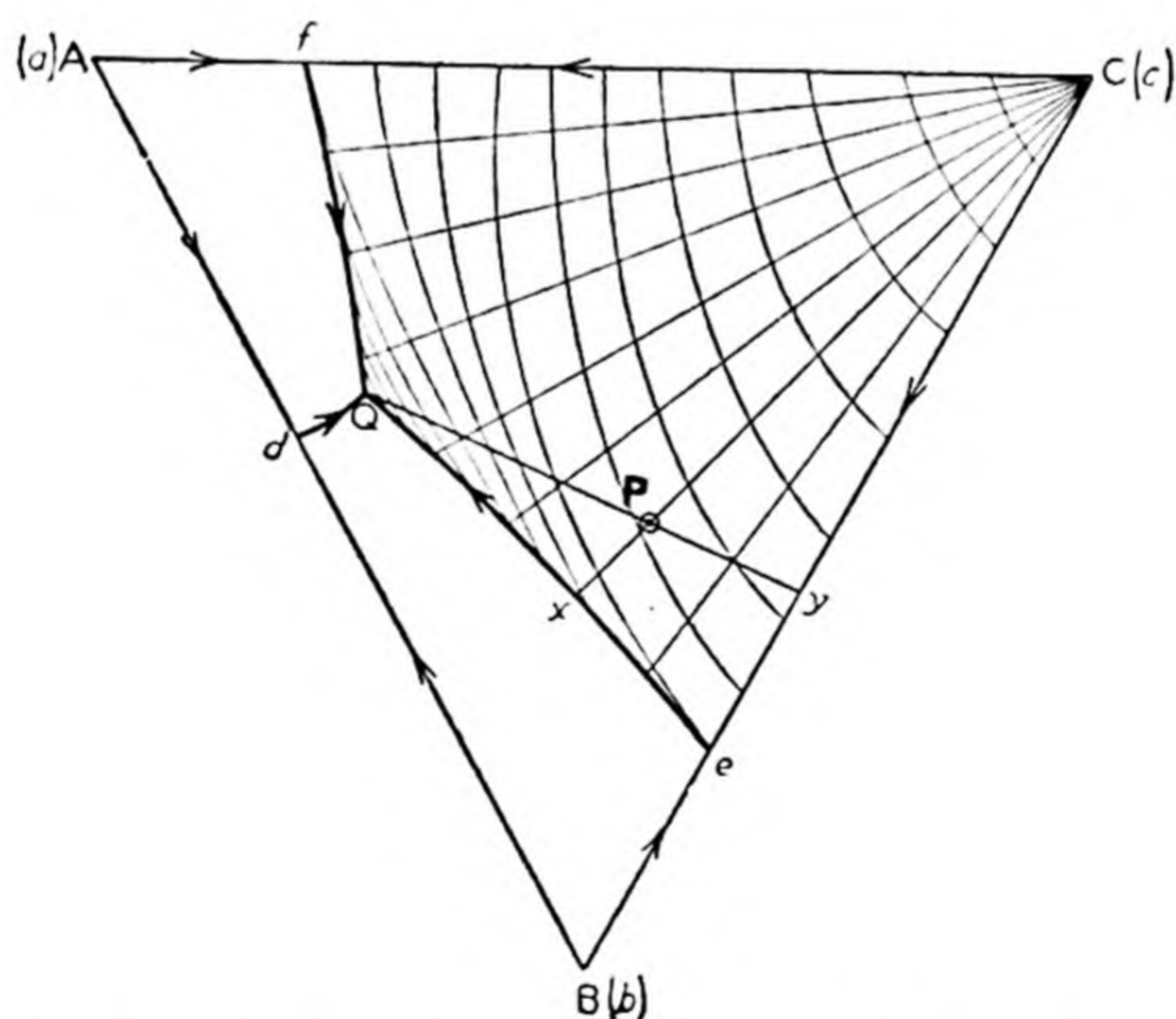


FIG. 16-18. Jänecke projection of Fig. 16-11 on the base ABC.

In projections on faces other than the base of Fig. 16-11, the curves of twofold saturation may cross, the fields overlapping, as seen in Figs. 16-14 and 16-15. But on all projections including those on the base, the actual surfaces are not shown, and it may be possible, in projections such as Figs. 16-13 and 16-18, for the actual C surface, for example, to overlap the A field

or the B field, although such overlapping is not shown on the projections. This would be the case if the C surface of Fig. 16-11 has a retrograde form such as that shown in section in Fig. 16-19, a vertical section of the tetrahedron from the WC edge to the face AWB. According to Fig. 16-19 the C surface would overlap one of the boundaries eQ , fQ , both in the orthogonal and in the Jänecke projections on the base ABC. Such relations, however, are not ordinarily encountered, and the fields of a Jänecke projection such as Fig. 16-18 are usually assumed to be mutually exclusive, the surfaces not overlapping in projection.

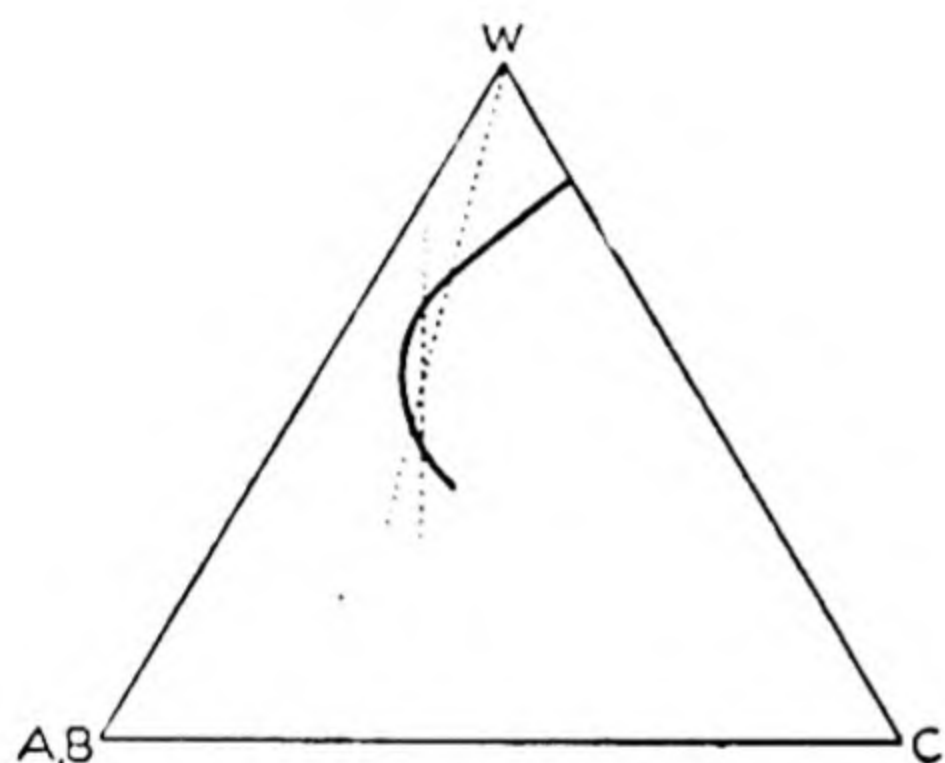


FIG. 16-19. Retrograde course of a solubility surface.

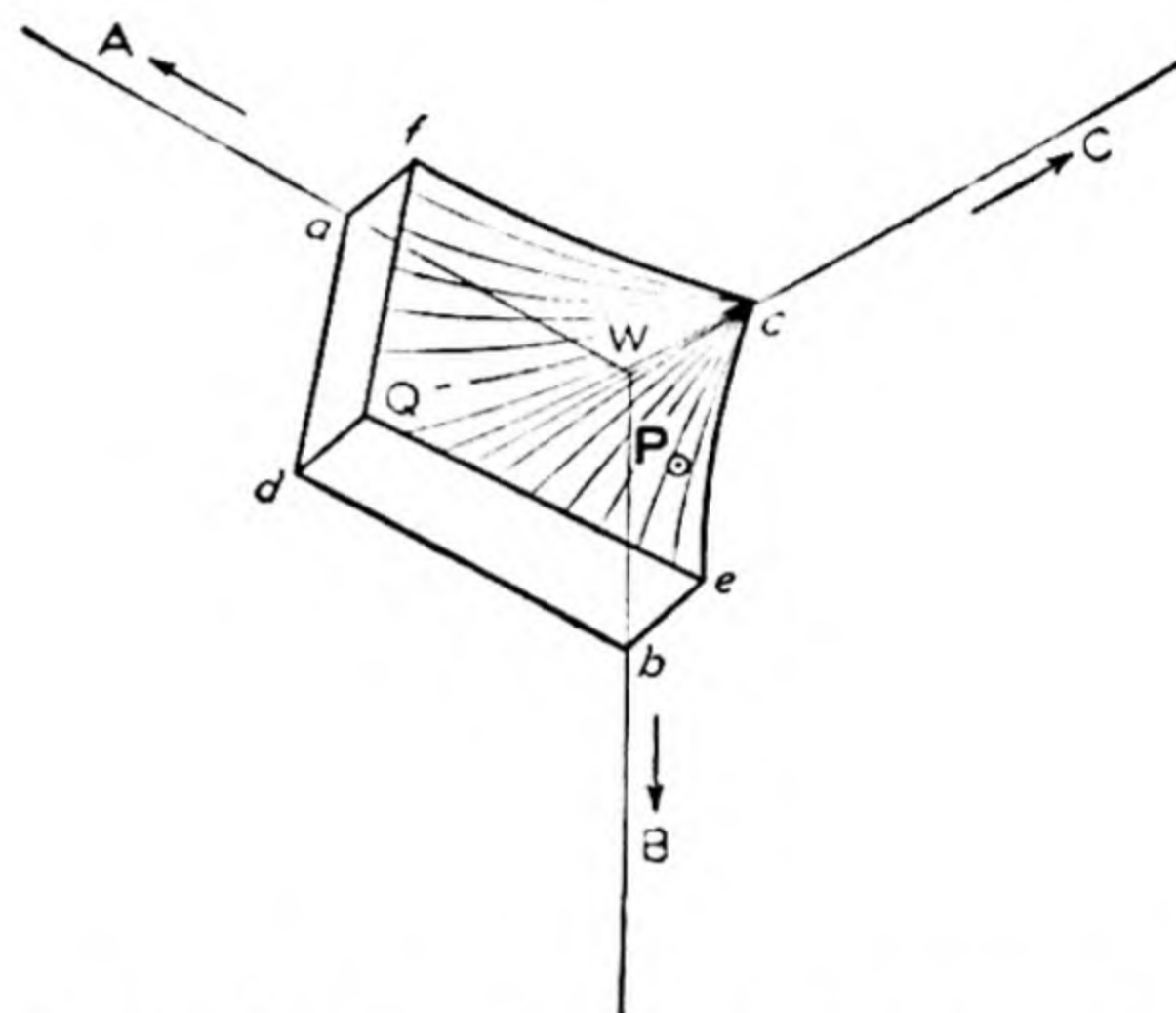


FIG. 16-20. Löwenherz diagram of Fig. 16-11.

Finally, Fig. 16-20 shows the compositions of Table I plotted on a Löwenherz diagram, the data being taken as grams of each salt per 100 g H_2O .

c. *Interrelations of the projections.* Fig. 16-21 combines in one triangle three projections of the isothermal curves. The points and curves with the subscript 1 (diagram 1) are the Schreinemakers projection of Fig. 16-16 on the face $A_1(W, B)_1C_1$. Those with subscript 2 are the Schreinemakers projection on the face $A_2B_2(W, C)_2$. The primed points and curves are the Jänecke base projection, on $A'B'C'$. The latter may be constructed from the others as explained under Fig. 16-4. Thus point d' is obtained by extending Cd_2 to the AB side, and j' by extending Bf_1 to the AC side. Q' is the intersection of BQ_1 with CQ_2 . Point e' is fixed by the method of parallels, whereby an arbitrary straight line through B (or C) is used to divide the side BC into segments proportional to Be_1 and e_2C . In Fig. 16-21, $Bm = Be_1$ and $mn = e_2C$; me' is then drawn parallel to nC . The point P' , the Jänecke projection of P on the base ABC, is fixed from P_1 and P_2 , as Q' is fixed from Q_1 and Q_2 .

Fig. 16-22 is a similar superposition of orthogonal and Jänecke projec-

tions on the base ABC. The graphical relation was explained under Fig. 16-2. The points d' , e' , and f' are fixed by merely extending the lines Wd , We , and Wf , to the sides of the triangle, and Q' is constructed from Q as

explained in Fig. 16-2, by extending WQ so that

$$100 \frac{QQ'}{WQ'} = \%W.$$

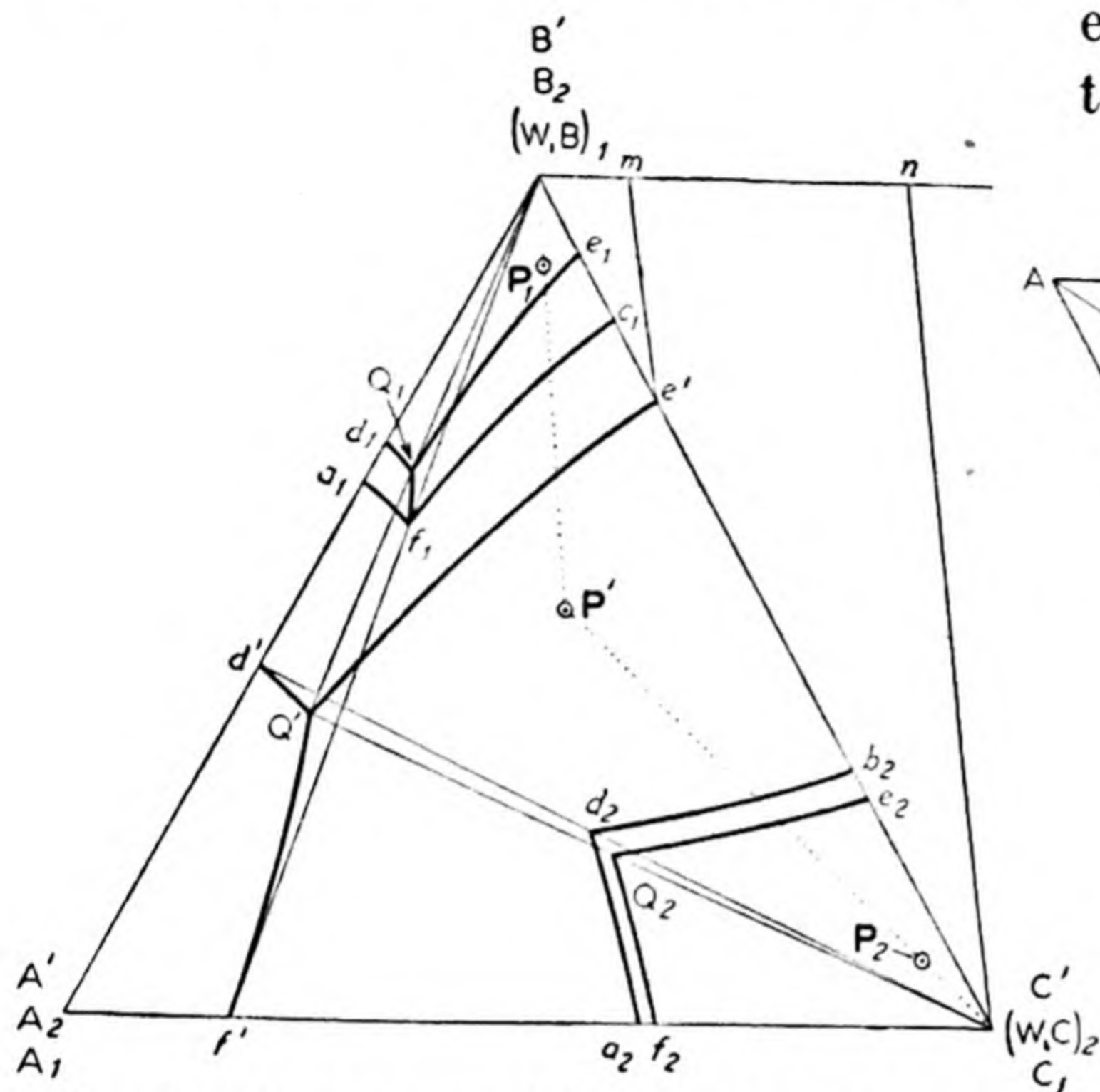


FIG. 16-21. Superposition of Schreinemaker and Jänecke diagrams.

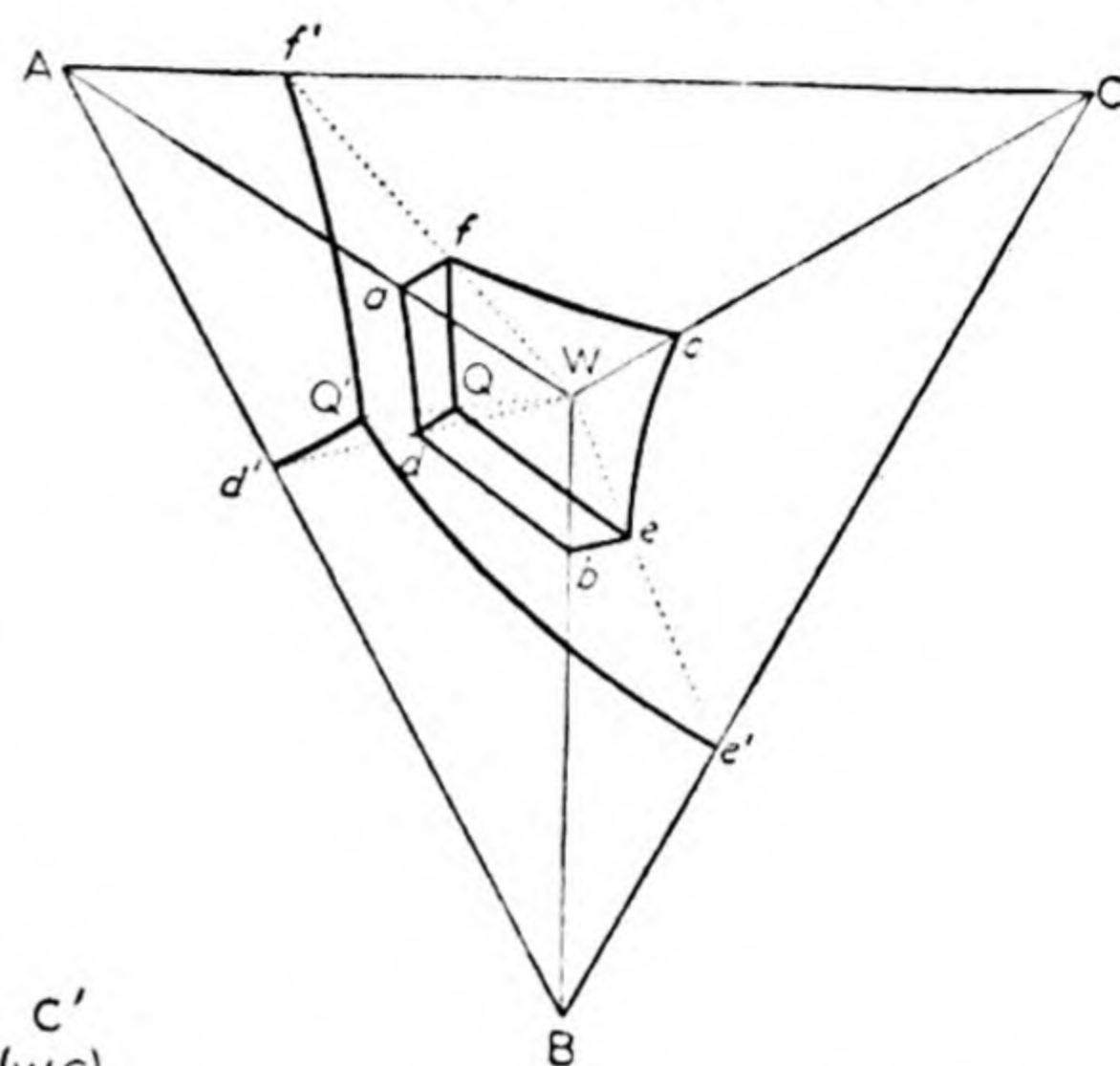


FIG. 16-22. Superposition of orthogonal and Jänecke projections on base.

Since the Löwenherz diagram is not comparable in units with the tetrahedral diagram, we may superimpose a Löwenherz diagram and a Jänecke

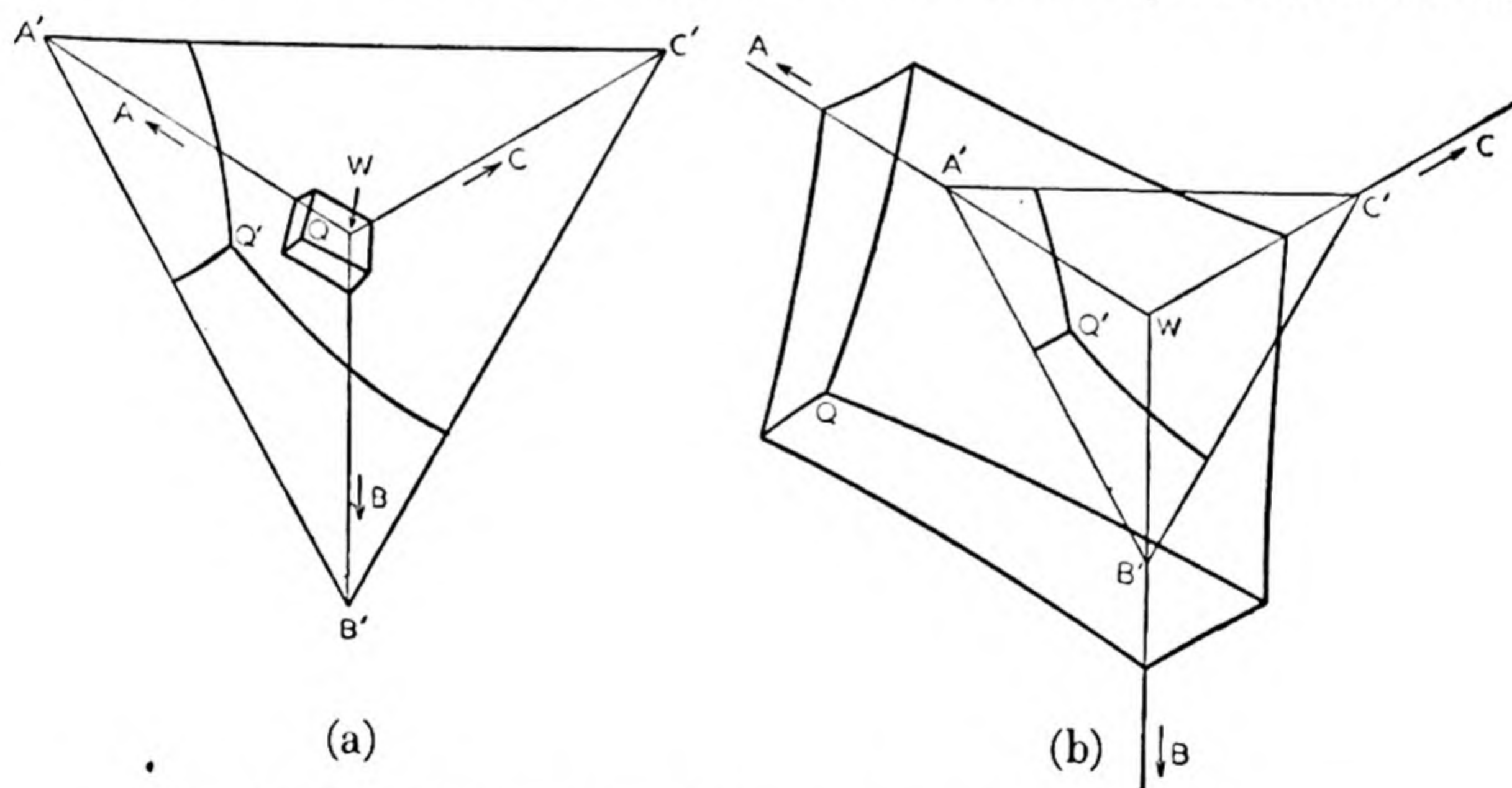


FIG. 16-23. Superposition of Löwenherz and Jänecke diagrams.

base projection, but there is no connection between their scales. Fig. 16-23 shows two possible arbitrary superpositions. The Löwenherz and Jänecke points lie on the same line through W , but there is no general connection

between their relative distances from W and the water content of the point. The relation varies from point to point as N , the total weight of salts per 100 grams of water, varies. The water content ($\%W$) = $100 \text{ PP}'/\text{WP}'$ only for that point for which $N = (S/\sqrt{3}) - 100$, S being the length of the side of the Jänecke diagram.

2. Isothermal Evaporation

a. *Fig. 16-11 and its sections.* If the unsaturated solution P of Fig. 16-11, consisting of water and three non-volatile salts, is evaporated at constant T , the composition of the system (condensed phases) changes along a line fixed by the points W and P , the original composition of the solution. If the extension of this line pierces the C surface, as at point v in Fig. 16-11, C is the first salt to precipitate. The value of the water content, and with it the composition of the solution at which saturation with respect to C is reached (point v), can be determined from a section of the tetrahedron including the line WP . As C precipitates, the liquid composition moves on the C surface following a curved course (a "crystallization path") defined by the intersection with the C surface, of the plane PWC passing through P and the edge WC . The liquid composition moves away from the edge WC with

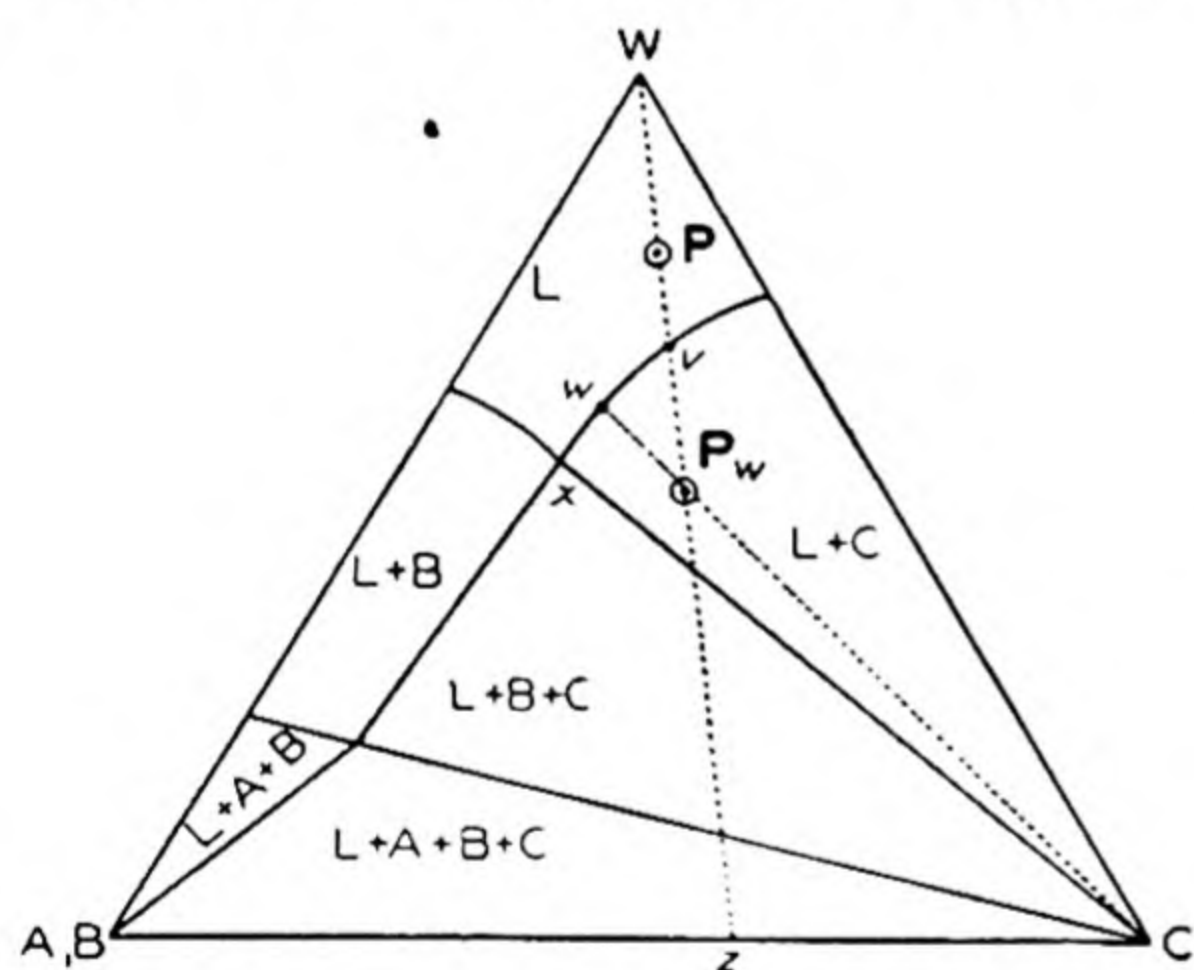


FIG. 16-24. Section of Fig. 16-11.

decreasing water content W_i (strictly vapor pressure) of the saturated solution, because it is losing both W and C . (With a retrograde effect of W_i on the solubility of C , as in Fig. 16-19, the concentration of C may increase, at equilibrium, as evaporation proceeds, but the crystallization path is still fixed by the intersection of the plane PWC with the C surface.) The liquid finally reaches one of the curves eQ or fQ . If it reaches eQ , at point x , it begins to precipitate B with C , and as it now loses W , B , and C , it proceeds on the curve eQ away from the face BWC , to point Q , where it dries up invariantly (at constant W_i and fixed composition) to a mixture of $A + B + C$.

b. *Separation of single solid phase.* The relative amounts of liquid and solid C , while the liquid moves on its course vx on the C surface, may be found from the tie-line connecting liquid and C , for any specified value of the water content, either of the solution or of the total complex. This may be done graphically on a section of the tetrahedron corresponding to the plane PWC (Fig. 16-24), which shows the points v and x of Fig. 16-11.

When the water content of the liquid reaches the value w , the total composition of the condensed phases ($C + L$) is P_w , and the ratio $C/L = wP_w/P_wC$. In any section through W and the base of the tetrahedron, $\%W$ is merely the vertical height relative to the altitude as 100%: at P_w , that is, $\%W = 100 zP_w/zW$. Similarly, then, the composition of the liquid, point w , and the phase ratio may be determined from this section for a specified value of water content of the total system, or point P_w . The total composition P_w is always the intersection of the tie-line wC with the line WP_z .

If two points on these tie-lines are known, such as the composition of the liquid and a total composition or wet residue ($L + \text{solid phase}$), then the

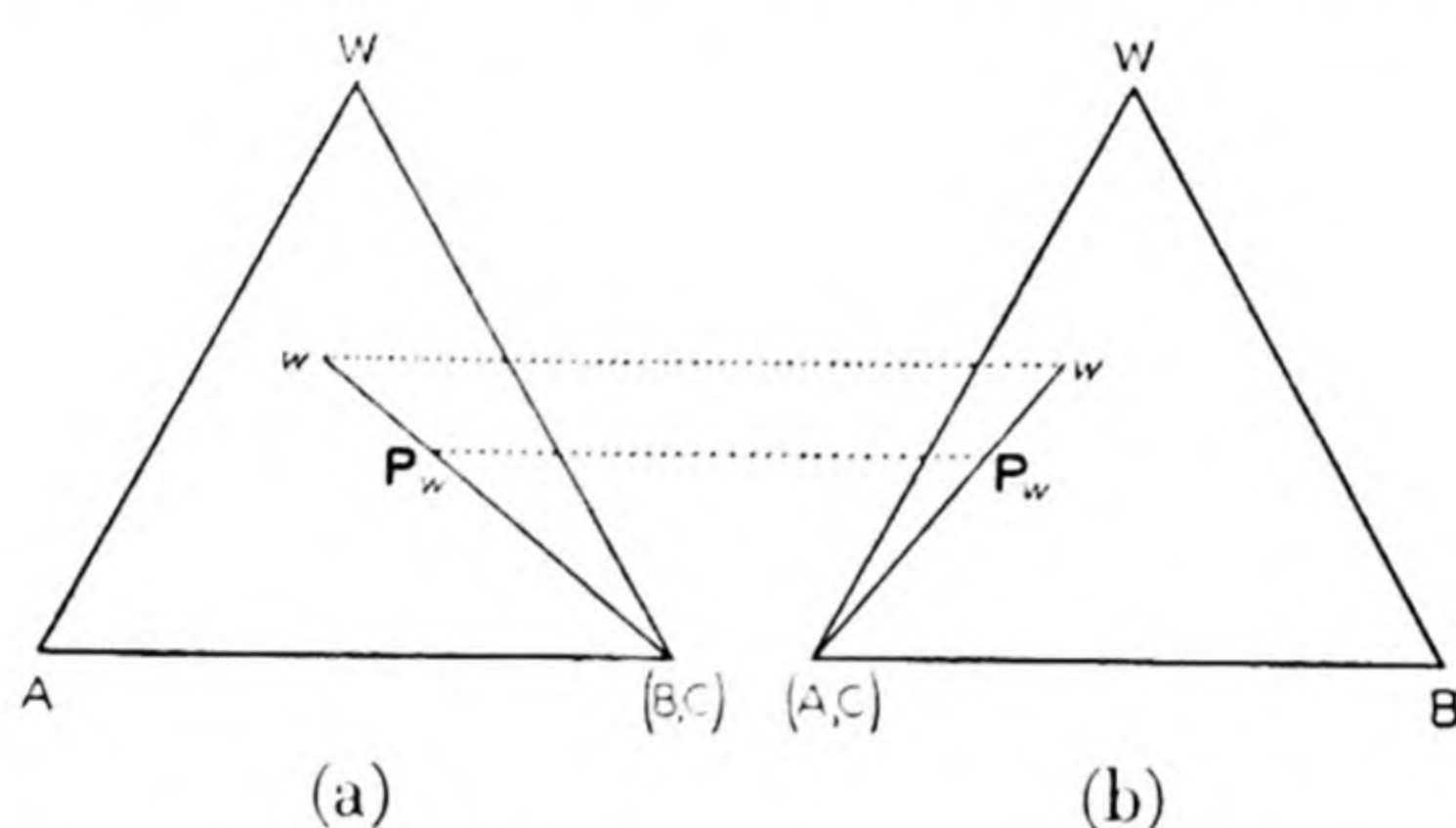


FIG. 16-25. Extrapolation of tie-lines on two Schreinemaker projections.

intersection of such tie-lines may be used in the usual way to identify the solid phase. This is best done by plotting the data on a suitable pair of projections, so that the composition of the intersection may be determined graphically. Fig. 16-25 shows the tie-line $P_w w$ of Fig. 16-24 plotted on a pair of Schreinemaker projections, which is probably the most convenient type for this purpose, one on (a), the plane $AW(B, C)$, the other on (b), the plane $(A, C)WB$. If a family of tie-lines, all involving a single, continuous surface of the tetrahedron, intersects at the corner (B, C) in (a) and at (A, C) in (b), the solid phase is pure C , since it is evident that the solid is anhydrous, containing no A , according to (a), and no B , according to (b). The point of intersection in (a) fixes $\%A$, that in (b) fixes $\%B$, and either one gives $\%W$, in the solid. If the solid is a solid solution, as of C and B , the tie-lines will intersect at the corner (B, C) in (a), but will cover a range of the base of (b). For a hydrate of C , the convergence will be at a point on the side $W(B, C)$ in (a) and on the side $W(A, C)$ in (b). For an anhydrous double salt of A and C , the lines would converge at a point on the base of (a) and at the corner (A, C) in (b). Such graphical identification may be made by means of a suitable pair of projections of any type, but the ratio of the quantities of the liquid and solid phases will be given by the inverse ratio

of the tie-line segments only on a non-perspective projection, such as either of those of Fig. 16-25.

c. *Crystallization paths of single precipitation.* As stated earlier, the course followed by a liquid precipitating C during isothermal evaporation is determined by the intersection with the C surface of a plane fixed by the edge WC. These paths radiate from the point *c* in Fig. 16-11 and lead to the curves *eQ* and *fQ*. On the orthogonal base projection (Fig. 16-13) these paths are curves coincident with *ce* and *cf* at the ternary boundaries, only one being a straight line, the line *cW* extended to the curve *eQ*. A projection such as this then is not in general very useful for the consideration of isothermal evaporation. A dilute solution with composition near point W of the tetrahedron of Fig. 16-11 will of necessity be plotted in the C field of this orthogonal projection. But isothermal evaporation of the solution will not necessarily lead to a point on the C surface of Fig. 16-11. Furthermore, if we do know the field first reached, as the C field at point P_1 of Fig. 16-13, we cannot from the projection alone predict which of the curves *eQ*, *fQ* it will reach on further evaporation, because of the unknown curvature of the projected crystallization paths. The same deficiencies pertain to the much used Löwenherz diagram, Fig. 16-20.

These difficulties are absent in the Jänecke base projection, or the "Jänecke diagram," Fig. 16-18. A dilute solution with salt proportions **P** will (in the absence of unusual retrograde curvatures of the solubility surfaces) precipitate C as the first salt upon isothermal evaporation, because **P** lies within the C field of the Jänecke diagram. As C precipitates, the composition of the solution moves on a rectilinear crystallization path, **CP**, away from C. Since only the proportions of salts are plotted, the corner C represents pure C, a hydrate of C, or its pure solution, saturated or not. (These crystallization paths cut contours of decreasing "water content," or strictly of decreasing vapor pressure, as they radiate from C.) In the case assumed, then, the solution must reach the curve *eQ* at point *x*, and there begin to precipitate B together with C. As the solution then travels on the curve *eQ* toward Q, the composition of the mixed solids ($B + C$) in equilibrium with the liquid will be given by the straight line from the curve, through **P**, extended to the side BC. When point Q is reached, therefore, the equilibrium solids will consist of B and C in the proportion given by point *y*. As the liquid Q finally dries up, invariantly, the solid composition moves on the straight line from *y* to **P** to leave $A + B + C$ in the proportions **P**.

d. *Jänecke prism.* The relative amounts of the phases at any point in the process cannot be read from the Jänecke tie-lines, since the water content is neglected in the plotting. The phase ratios may be calculated, but

not determined graphically, in an approximate fashion, if the diagram contains an adequate number of contours of water content, or if the Jänecke base is combined with elevations for the representation of water content. Thus with Fig. 16-18 as the base and with water content represented as a perpendicular dimension at every point, we obtain a triangular prism (Fig. 16-26) known as a Jänecke prism, similar in schematic appearance to Fig. 12-16, the isobaric T/c prism of a simple ternary system involving pure solid phases. This shows again the analogy between the variable of temperature at constant pressure, and the variable of W_l ("water content" of saturated solutions, but strictly their vapor pressure) for an aqueous system of next higher order at constant temperature, and involving non-volatile salts. This was pointed out in Chapter XIII, the condensed ternary isotherms of Figs. 13-14 and 13-18 being similar to binary isobars, with the variable " W_l " as the analog of T . In the present case the Jänecke prism, representing the condensed isotherm of a quaternary aqueous salt system, involves relations of the solubility surfaces analogous to those in the isobaric T/c ternary prism, again with the variable " W_l " in place of T . The Jänecke projection (Fig. 16-18) may be called the "polyhydric projection" of this prism, and is the analog of the ternary polythermal projection (Fig. 12-18). In the latter diagram E, the temperature minimum, is the crystallization end-point on cooling; in the present Fig. 16-26 Q is the crystallization end-point on isothermal evaporation, and it is the minimum in vapor pressure, and usually also in actual water content. But again, even in Fig. 16-26 the tie-line ratios will not give the phase ratios, since there is no point representing water, or component D, itself, in this prism.

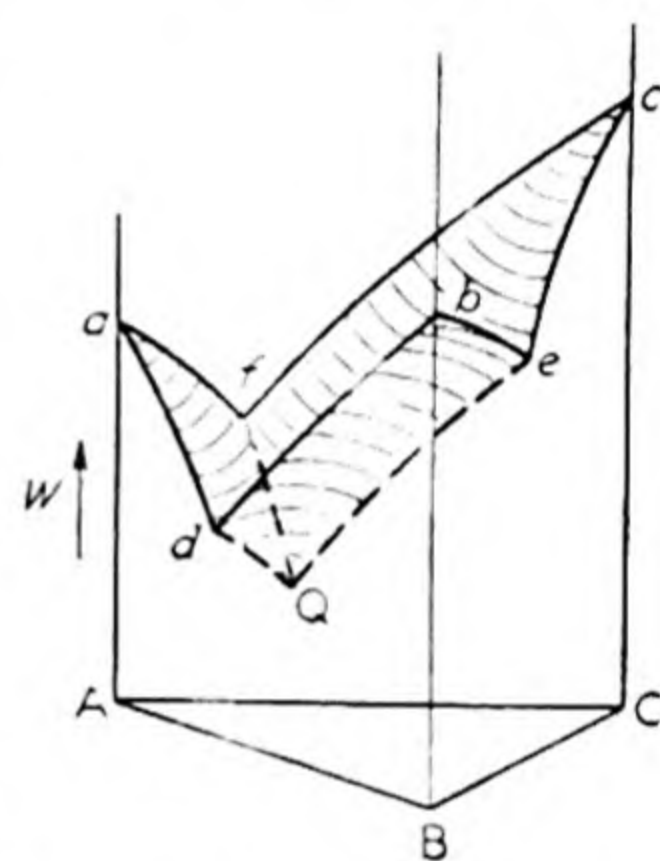


FIG. 16-26. Jänecke prism for Fig. 16-11.

e. *Combinations of projections; graphical considerations.* We return now to the consideration of the crystallization paths for liquids traveling on a surface of saturation with respect to one solid during isothermal evaporation. For the C surface this path is the intersection of the plane WPC with the surface, and its projection is a straight line only on those projections in which the plane WPC is itself a straight line, namely, on the Jänecke base ABC, the Jänecke projection on AWB, the Schreinemakers projection on AB(C, W) and the semiperspective projections from the WC edge upon AWB or ACB. Hence any of these projections may be used to find point x , the intersection of the plane WPC with the curve eQ , as seen in Fig. 16-18. But of all these only the Jänecke base, or the Jänecke diagram, has the special advantage that the "total composition" remains at a fixed point

during the process of isothermal evaporation, since the projection involves only the salt proportions. This is the reason for the importance of this particular diagram. In order, however, to carry out graphical determination of phase ratios from tie-line segments, the Jänecke diagram must be combined with a non-perspective projection.

For the quantitative graphical consideration of the isothermal evaporation of a given solution (an unsaturated solution of composition P , that is), the most generally useful combination is therefore the Jänecke base and

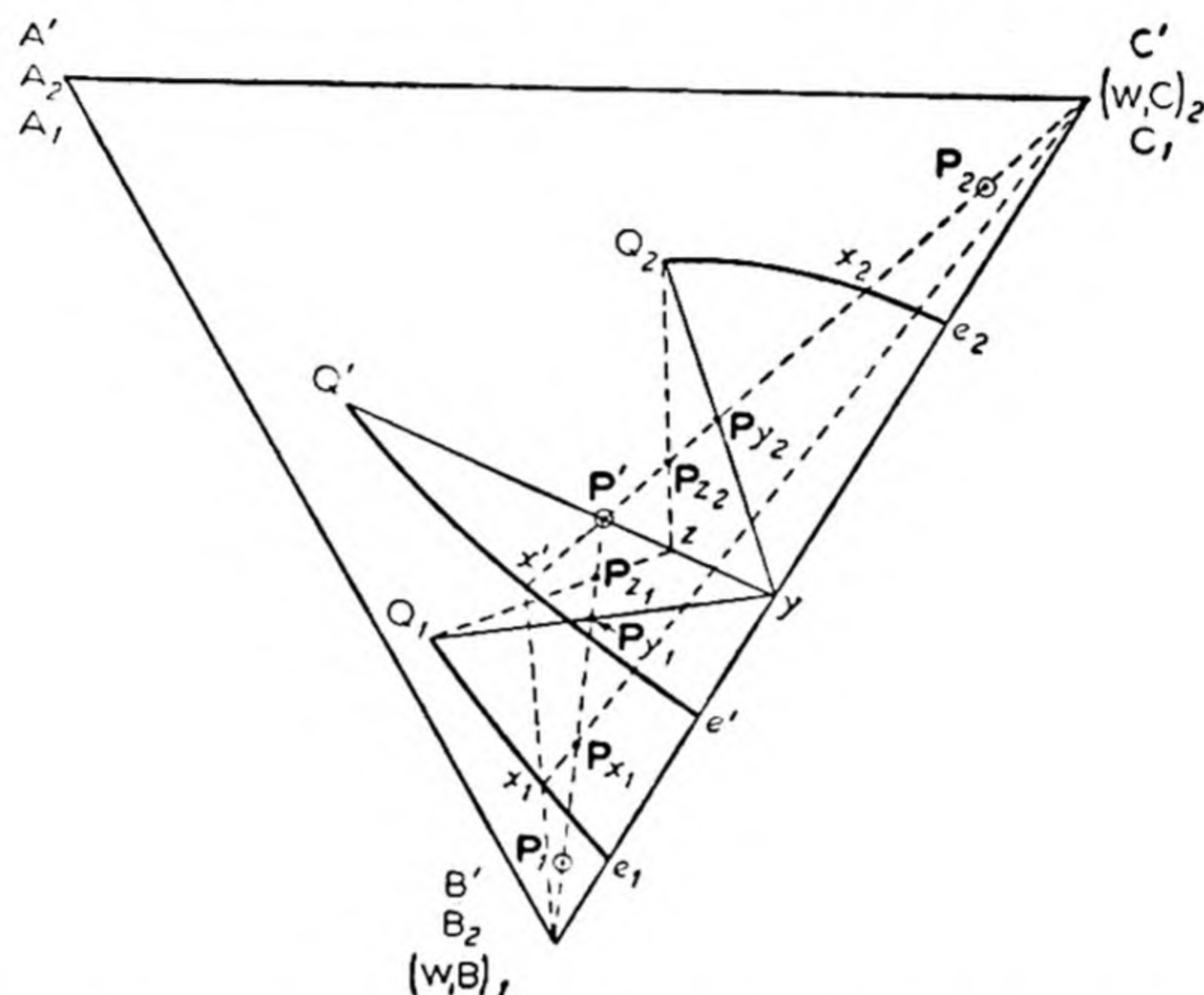


FIG. 16-27. Use of superposed Schreinemakers and Jänecke projections for graphical operation.

some orthogonal or some Schreinemakers diagram. Graphical construction applies, however, only for processes involving quaternary curves and points, for saturation with two or three solids, since the projected diagrams do not in general represent the surfaces themselves except in approximate fashion by means of contours. The Jänecke diagram (Fig. 16-18) therefore shows that the first salt to precipitate from the solution P will be C and the second B , at point x ; but the actual concentration (water content) at which saturation with C is reached, at point v of Fig. 16-11, cannot be determined, except approximately from contours, from any projection, but requires sections of the tetrahedron, such as Fig. 16-24. The same is true for the quantitative relations during the course of the liquid on the C surface from v to x . Once the point x is reached, however, on the twofold saturation curve eQ , the course of isothermal evaporation may be followed quantitatively by graphical operations.

Fig. 16-27 shows three projections of the curve eQ (and of the solution P): e_1Q_1 , a Schreinemakers projection on the triangle $A_1(W, B)_1C_1$; e_2Q_2 , a

on the intersection of Wx' with e_1Q_1 , at x_1 , and the water content of L_x is $\%W = 100x_1x'/Wx'$. The orthogonal projection of the total composition is P_{x_1} , the intersection of x_1C with WP' ; its water content is $\%W = 100 P_{x_1}P'/WP'$, and the ratio of solid C to $L_x = x_1P_{x_1}/CP_{x_1}$. When the liquid just reaches point Q, the solid is a mixture of B and C at point y , fixed by

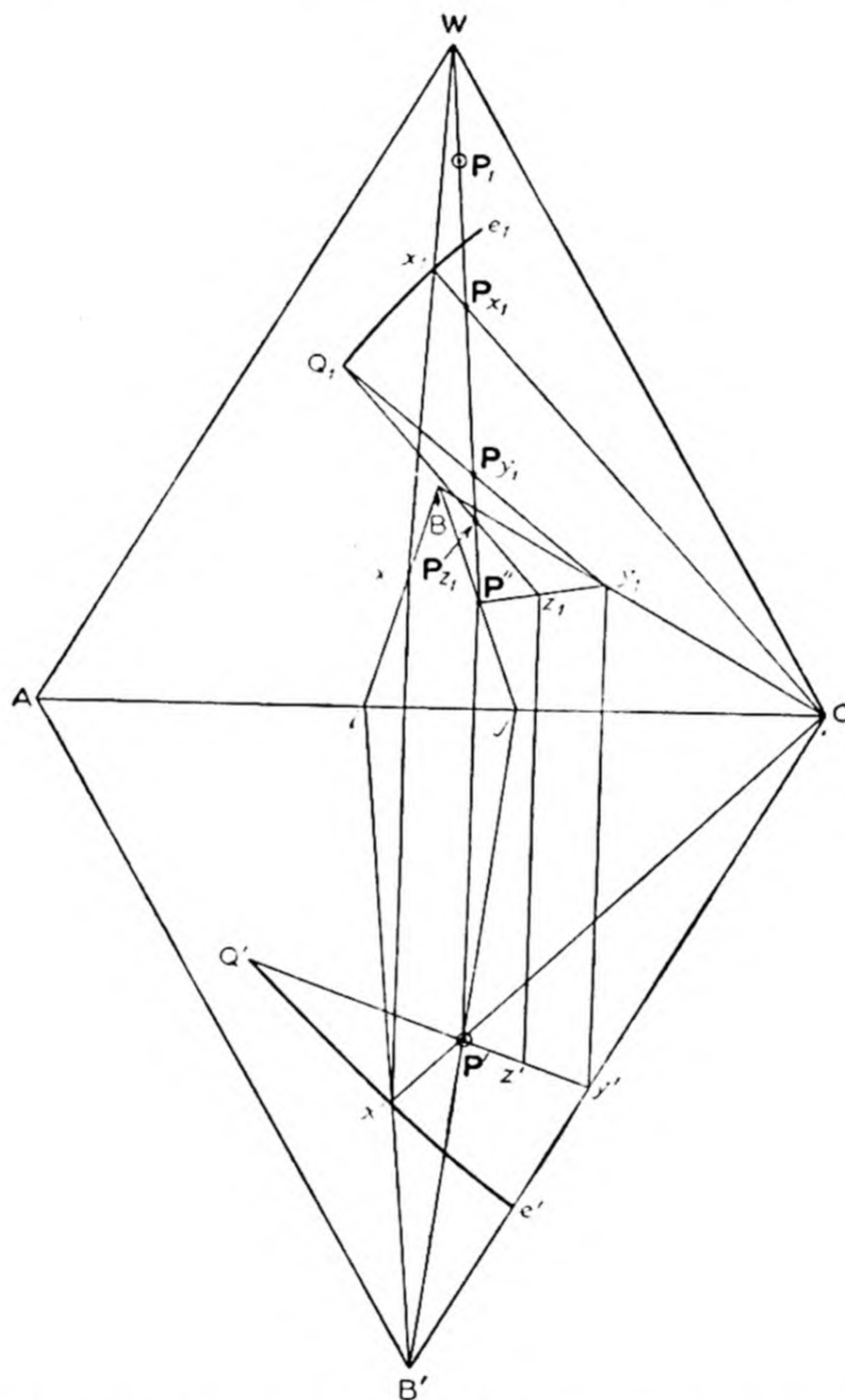


FIG. 16-29. Graphical operation with Jänecke base and orthogonal projection on a face.

the line $Q'P'$ extended to BC . The total composition is P_{y_1} in orthogonal projection, the intersection of Q_1y with WP' . When the total composition reaches P_{z_1} , with $\%W = 100 P_{z_1}P'/WP'$, the solid is a 3-phase mixture of composition z , the intersection of the extension of $Q_1P_{z_1}$ with $P'y$. The ratio of solids to L_Q is always given by the inverse ratio of the segments of the orthogonal projection of the tie-line through total composition.

In a manner similar to that of Fig. 16-28, the Löwenherz point for solu-

tion x may be found on one of the diagrams of Fig. 16-23. With x' fixed by the Jänecke diagram the intersection of $x'W$ with the Löwenherz plot of curve eQ gives x_1 , the position of L_x on the Löwenherz diagram. But further consideration of the isothermal evaporation is not possible with this diagram since there are no tie-lines in the Löwenherz plot.

In Fig. 16-29 the same process is followed by means of the combination of Jänecke base (lower diagram) and an orthogonal projection on the face AWC. The Jänecke point x' is now transferred to the orthogonal by the construction explained under Fig.

16-6. $B'x'$ is extended to i , and x'' is fixed on iB by a vertical from x' .

The intersection of $x''W$ with e_1Q_1 gives x_1 as the orthogonal projection of the point x' . Like x'' , P'' is transferred from P' . Now the line WP''

gives the total composition, orthogonally projected, during evaporation of water. Hence with the liquid at x_1 and saturated with C, the total composition is at P_{x_1} and the ratio

$C/L_x = x_1P_{x_1}/P_{x_1}C$. When the liquid has just reached Q, the solid is B + C at y' ; transferred vertically to the line BC, this gives y_1 in the orthogonal diagram. The total composition is now at P_{y_1} , the intersection of Q_1y_1 with WP'' . When the total composition reaches P_{z_1} , the solid is at z_1 on the line $P''y_1$, and the composition at z_1 is read from its Jänecke

projection z' , transferred vertically from z_1 to the line $P'y'$. Again the phase ratios are read from the segments of the tie-lines in the orthogonal projection.

Very similar construction is used in Fig. 16-30, combining the square orthogonal ABCW with the Jänecke base AB'C. The Jänecke point x' is transferred to the orthogonal diagram to fix the point x_1 on curve e_1Q_1 , as explained under Fig. 16-7. Point a is on the extension of CP' , ab is a vertical to AB, and P'' is on bC , vertically above P' . Now the orthogonal projection of the total composition lies on the line WP'' as water is evaporated. Hence P_x is fixed as the intersection of WP'' with x_1C . For the water content of a point such as L_x , appearing on both projections,

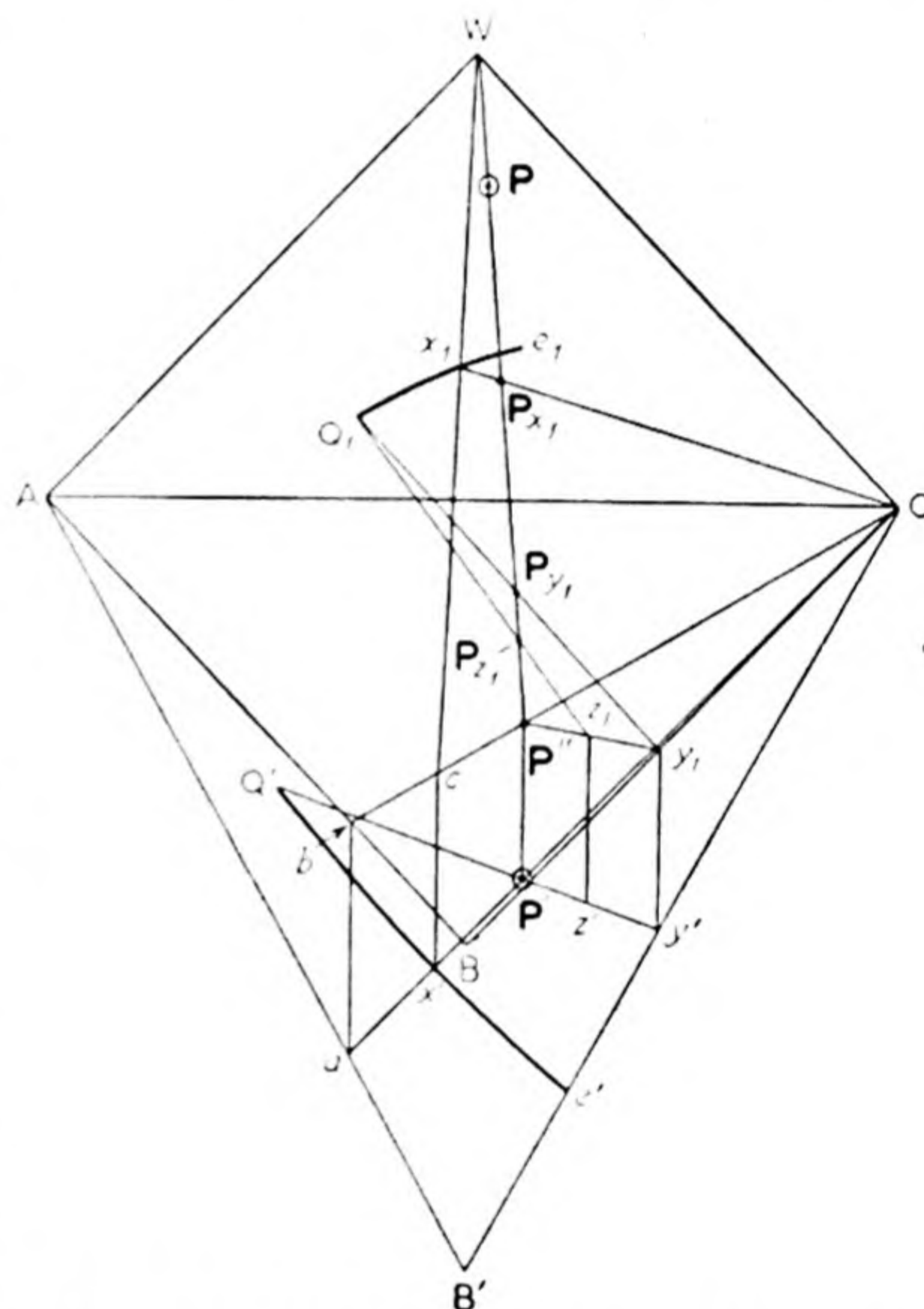


FIG. 16-30. Graphical operation with square orthogonal projection and Jänecke base.

Point a is on the extension of CP' , ab is a vertical to AB, and P'' is on bC , vertically above P' . Now the orthogonal projection of the total composition lies on the line WP'' as water is evaporated. Hence P_x is fixed as the intersection of WP'' with x_1C . For the water content of a point such as L_x , appearing on both projections,

$\%W = (B' + 2Y)/(1 + B'/100)$, in which B' represents the quantity of B in the Jänecke plot and Y is the vertical distance of x_1 above the line AC, in terms of $AC = BW = 100$, as explained under Fig. 16-3. When the liquid has just reached Q, the solid mixture of B + C is fixed at y' on the Jänecke diagram, as usual. This is transferred vertically to y_1 on BC as its orthogonal projection, and the total composition is now P_{y_1} . When the total composition reaches P_{z_1} , the solid (A + B + C) is at z_1 and its composition is read from the Jänecke point z' .

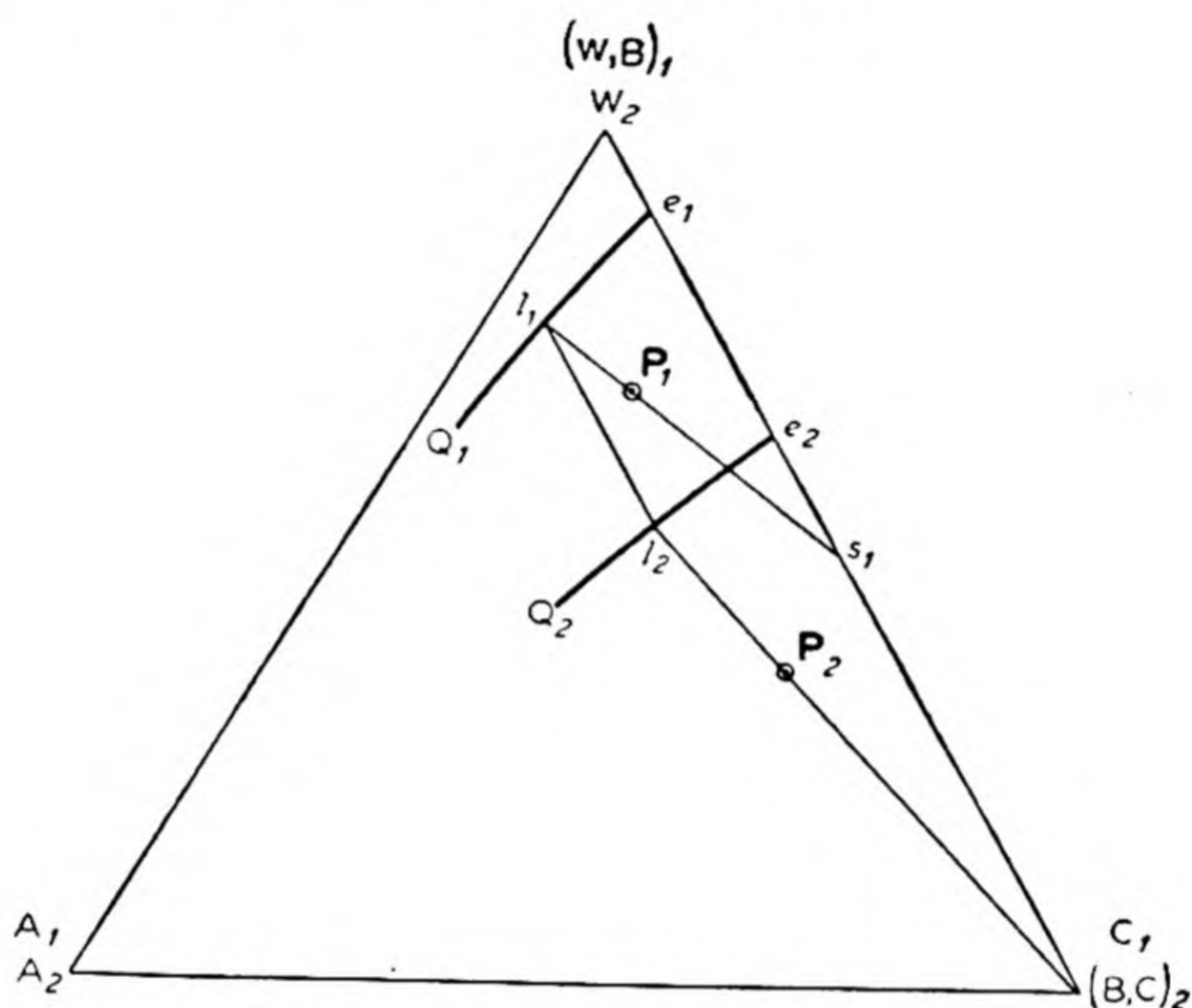


FIG. 16-31. Graphical operation with two superimposed Schreinemakers projections.

On all these diagrams (Figs. 16-27 to 16-30) the liquid is saturated with two solids if the total composition lies between P_x and P_y . It is saturated with three solids, and therefore invariant, if the total composition lies between P_y and P' in Figs. 16-27 and 16-28, and between P_y and P'' in Figs. 16-29 and 16-30.

Fig. 16-31 deals with the special problem of finding the liquid composition l , on the curve eQ , for a specified total composition, P , of the condensed system ($L + 2$ solids, B and C); P is therefore a point in the space of Fig. 16-12(b). The figure shows two Schreinemakers⁸ projections of the curve and P : e_1Q_1 and P_1 on the plane $A_1(W, B)_1C_1$, and e_2Q_2 and P_2 on the plane $A_2W_2(B, C)_2$. The second projection is chosen so that the plane BCP ap-

⁸ W. N. Lodochnikov's method of representation (*Ann. Inst. Anal. Phys. Chim., U.S.S.R.*, **2**, 255, 1924; *Z. anorg. Chem.*, **151**, 185, 1926; **169**, 177, 1928) is equivalent to the superposition of two of the projections here called the Schreinemakers. This was pointed out in a discussion of the method by M. Randall and B. Longtin, *J. Phys. Chem.*, **42** 1157 (1938).

pears as a straight line; with the solid mixture given by the corner $(B, C)_2$, the liquid point, l_2 , may be fixed by the extension of the line $P_2(B, C)_2$. From l_2 we read $\%A$ and $\%W$ in l , and from l_1 , fixed by a line through l_2 parallel to the side WC , we read $\%C$, thus obtaining the required composition l . The line l_1P_1 is now extended to the side $(W, B)_1C_1$ to fix point s_1 , from which we read $\%C$ in the mixture of solids, $B + C$. Finally, the ratio of solids to liquid = l_1P_1/P_1s_1 or l_2P_2/P_2C_1 .

3. Effect of Temperature

The relations between a number of isotherms for the additive system consisting of water and three salts may be conveniently represented by a figure based on the Jänecke base diagram with T as a vertical axis. This gives a T/c prism in which the water content is ignored. The sides of this prism are the Jänecke projections of ternary systems of the type of Fig. 13-2, showing only salt proportions in each case. If the quaternary isothermally invariant points of threefold saturation for each set of three solids are then connected by continuous curves, the prism is divided into spaces with coordinates of T and salt proportions for solutions saturated with a single salt, surfaces (between adjacent spaces) for saturation with two salts, and curves for threefold saturation. The intersection of four such curves gives rise to a (condensed) invariant point for the equilibrium of solution + four solids (+ vapor).

D. Double Salts

The system $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$ at 75° is shown projected orthogonally on the base in Fig. 16-32(a) and perspectively, as a Jänecke diagram, in Fig. 16-32(b); both figures are schematic.⁹ The field abQ_2h is the projection of the solubility surface of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, point H in Fig. 16-32(a); cdQ_1Q_2b is the NaCl field; efQ_1d is the Na_2SO_4 field; and ghQ_2Q_1f is the field of saturation with burkeite, point D, $\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$. This double salt is congruently soluble in water (W) at this temperature, the line DW passing through its solubility curve in the ternary system $\text{Na}_2\text{SO}_4-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$ at the point g , which solution therefore contains the same ratio of these two salts as D itself. Hence D and g appear as the same point in the perspective projection (Fig. 16-32(b)). The crystallization paths for the D field radiate from point g , as curves in Fig. 16-32(a), as straight lines in Fig. 16-32(b). The curves fQ_1 , Q_1Q_2 , and Q_2h are solutions saturated with the pairs $\text{Na}_2\text{SO}_4 + \text{D}$, $\text{NaCl} + \text{D}$, and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + \text{D}$, respectively, and the points Q_1 and Q_2 are isothermally invariant solutions saturated

⁹ J. E. Teeple, *loc. cit.*, p. 71.

with three salts. Since each of these points falls inside the triangle of its three salts, as seen in Fig. 16-32(b) but not necessarily in Fig. 16-32(a), each is "congruently saturated" with respect to its three salts, and will be the congruent drying-up point for solutions with salt ratios in that triangle. If Q_1 should appear, as plotted in Fig. 16-32(a), just on the right of the line CD, we would not be able to determine, from the orthogonal projection alone, whether the proportions of its salts fall in or out of the triangle ACD. The only straight line crystallization path in the D field of Fig. 16-32(a) is that fixed by the line Dg and passing through W.

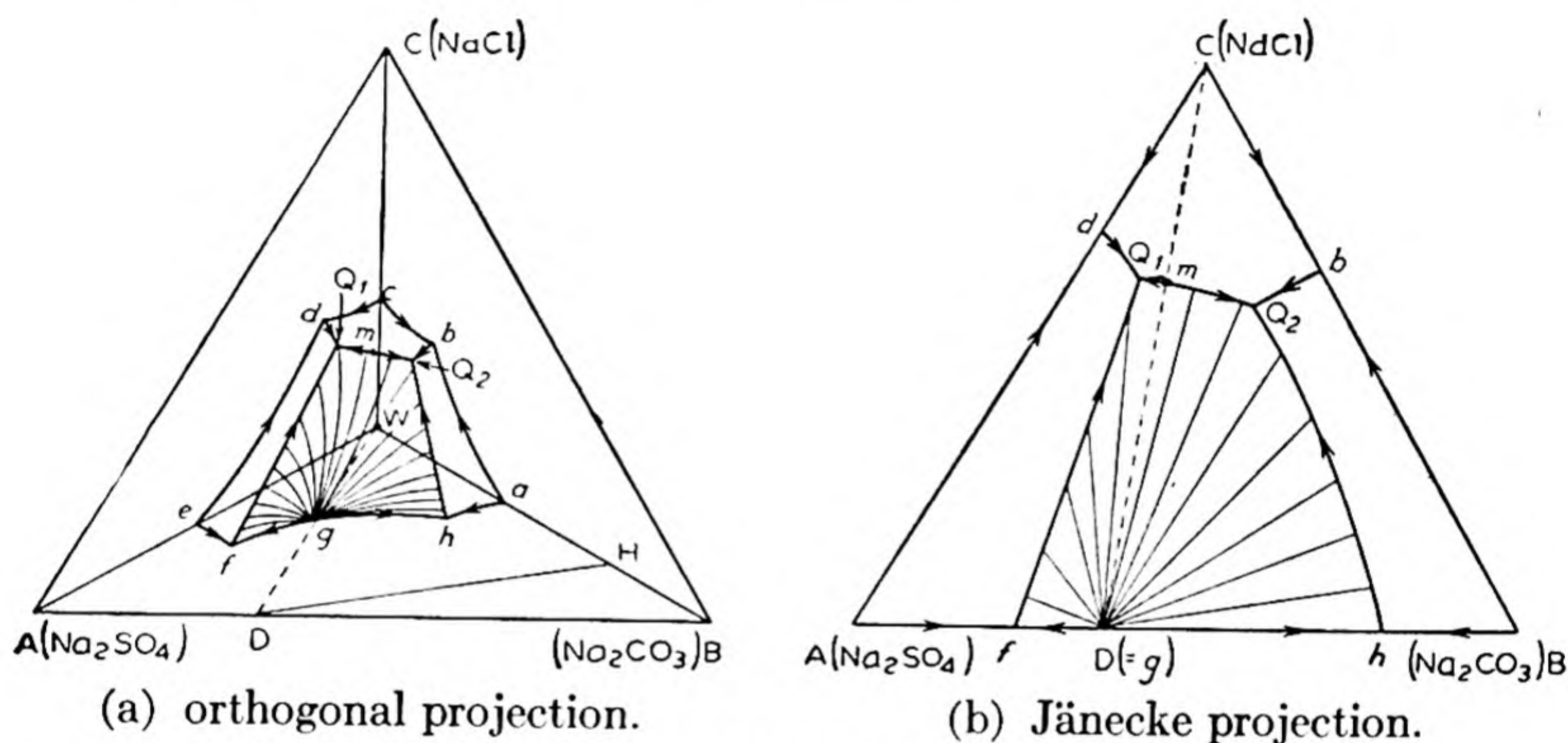


FIG. 16-32. System NaCl-Na₂SO₄-Na₂CO₃-H₂O, at 75°.

The course of the liquid along any curve in Fig. 16-32(b) is determined by the vectors of motion corresponding to the precipitation, on evaporation, of the two saturating salts. The course must be from f toward Q_1 , for example, because the solution loses simultaneously Na₂SO₄ and D. If point m then is the intersection of the line NaCl-D with the curve Q_1Q_2 , the course, as indicated everywhere by arrows, must be away from m on each side. The point m is therefore of the nature of a "saddle point," a point of maximum "water content" (strictly, of vapor pressure) on the curve Q_1Q_2 , and is said to be congruently saturated with respect to its two salts. The vertical section through CmD in the isothermal prism of the type of Fig. 16-26 is therefore a **quasi-ternary isothermal section**. A solution of composition m (that is, of salt proportions m) dries up invariantly to the salts NaCl + D. Point m is the intersection of the plane WDC with the curve Q_1Q_2 of the tetrahedron. The combination of the two diagrams, Figs. 16-32(a) and 32(b), may be used to determine graphically the intersection of any given plane through W and a curve on the orthogonal projection, thus fixing m on Fig. 16-32(a), as explained earlier for point x in Fig.

16-28. In the present case, if the diagrams are superimposed, the intersection of a line joining point m of the Jänecke diagram and W of the orthogonal diagram, with the curve Q_1Q_2 of the latter diagram, gives the required point m of Fig. 16-32(a).¹⁰

The arrows on the curves of Fig. 16-32(a), then, are placed there only after an analysis in terms of a Jänecke diagram, or after analysis in terms of the tetrahedral figure in three dimensions. The projection of Fig. 16-32(a) alone is not sufficient to establish, except in very obvious cases, whether an invariant point is or is not congruently saturated, or to determine the composition of a saddle point such as m , congruently saturated with two salts, on a quasi-ternary section of the isotherm.

If point Q_1 had fallen outside the triangle of its three salts, as in Fig. 16-33, it would be incongruently saturated with its three salts, and the "water content" (W_l) would fall continuously from Q_1 to Q_2 . Now Q_1 would not be a point of minimum W_l , and it would be the incongruent drying-up point for solutions in the triangle ACD . Solutions with salt proportions in this triangle must reach the point Q_1 since they must dry up to $A + C + D$, but at Q_1 the liquid is consumed in the reaction

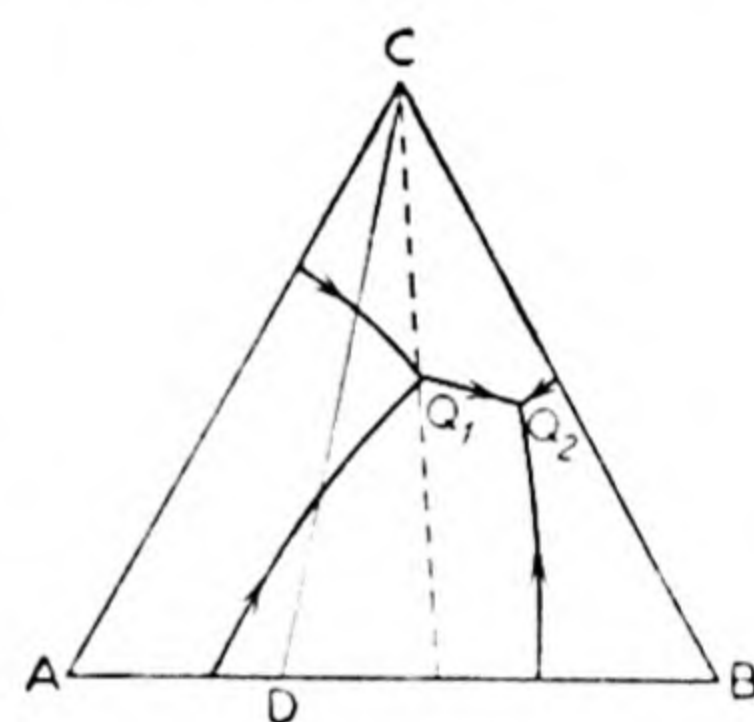


FIG. 16-33. Variation of Fig. 32(b).

$L(Q_1) + A \rightarrow C + D + H_2O$,[↗] leaving $A + C + D$.

Solutions reaching Q_1 from triangle DCQ_1 , however, lose the solid phase A at Q_1 , this salt re-

dissolving to leave the system $L + C + D$; the liquid then travels on the curve Q_1Q_2 , depositing more C and D , until it finally dries up, congruently

and invariantly at Q_2 , in the reaction $L \rightarrow C + D + B + H_2O$.[↗]

All the curves of Figs. 16-18, 16-32, and 16-33 are "even" curves, in the sense that they are curves of positive crystallization of the two saturating salts (for isothermal evaporation), but the invariant points involve positive crystallization of all three salts only if they are congruently saturated or lie inside the triangle of their three salts. Later we shall have cases in which the curves themselves may be "odd," in the sense that they are transition curves, along which one salt is dissolving at the expense of the other. If the solid A accompanying the solution reaching point Q_1 of Fig. 16-33 is removed or is not allowed to redissolve (isothermal evaporation with "effective removal of solid"), the liquid, coming from anywhere in the quadrangle ACQ_1D , must continue, of course, to Q_2 , to leave finally a deposit of four solids.

¹⁰ This procedure is explained by Blasdale (Ref. C), p. 123.

Comparison of Fig. 16-32(b) with Figs. 12-25(a) and 12-28, and of Fig. 16-33 with Fig. 12-25(b), brings out the analogy between the variable " W_l " for these quaternary isothermal projections and the variable T for the ternary polythermal projections.

Fig. 16-34 (a Jänecke diagram) shows the same system (NaCl – Na_2SO_4 – Na_2CO_3 – H_2O), still involving the same solid phases, at 35° , at which temperature the double salt burkeite is incongruently soluble in water. The

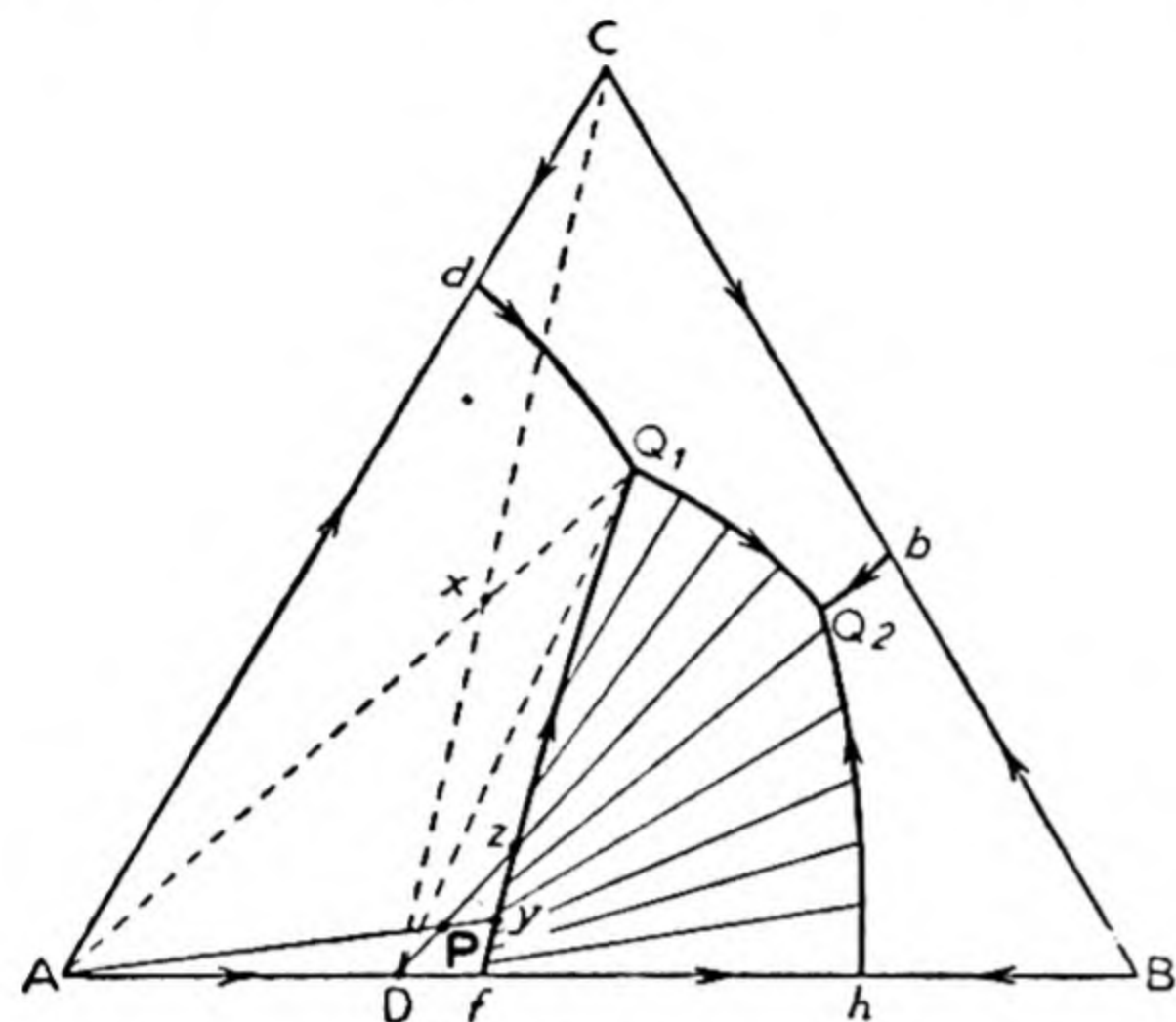


FIG. 16-34. System $\text{NaCl}(\text{C})$ – $\text{Na}_2\text{SO}_4(\text{A})$ – $\text{Na}_2\text{CO}_3(\text{B})$ – H_2O , at 35° .

point D now lies outside its field since it can saturate a ternary solution only in the presence of excess of B, above the ratio of B to A in D. But the crystallization paths still radiate as straight lines from the point D, as in the ternary polythermal analog of Fig. 12-34. On an orthogonal projection not only would these paths be curved, but their point of origin would be unknown, since there is no saturated solution of D alone containing the salts in the proportion D. In such cases the origin of the crystallization paths is usually estimated on

the basis of an extrapolation of the solubility curve of the compound (in its ternary system) to a metastable point of congruent solubility. Such an estimation in the case of Fig. 16-35, where D does not appear in the aqueous ternary system at all, is obviously very uncertain.

All the curves of twofold saturation except fQ_1 in Fig. 16-34 are still "even"; but the reaction on fQ_1 is "odd," being $\text{L} + \text{A} \rightarrow \text{D} + \text{H}_2\text{O}$, or $\text{A} - , \text{D} +$. Again all compositions in the triangle ACD must dry up to $\text{A} + \text{C} + \text{D}$ and must therefore reach Q_1 in isothermal evaporation. Those in $\text{AC}x$ reach it *via* the curve dQ_1 , carrying A and C as precipitating solids; those in AxD *via* the curve fQ_1 , along which A is dissolving at the expense of D. At Q_1 the invariant reaction is the same as for Q_1 in Fig. 16-33, and the liquid is consumed to leave $\text{A} + \text{C} + \text{D}$. Point Q_1 is similarly reached by solutions in $\text{x}CQ_1$ along curve dQ_1 and by solutions in $\text{D}xQ_1$ along the curve fQ_1 , but in both cases the A solid will be consumed at Q_1 since these solutions, in triangle DCB, must dry up at Q_2 to a mixture of $\text{D} + \text{C} + \text{B}$. With W_l as the analog of T (cf. Fig. 12-34), point Q_1 in both Figs. 16-33 and 16-34 is seen to be an invariant of type B (diagonal type, the invariant quadrangle being $\text{AC}Q_1\text{D}$) while Q_2 is of type A, terminal in respect to the liquid phase, which is the interior phase of the invariant triangle DCB.

Solutions in DfQ_1 reach the transition curve fQ_1 carrying solid A. But as the liquid then travels on this curve toward Q_1 during isothermal evaporation, and as the solid is transformed from A to D, a point is reached, before the liquid reaches Q_1 , when the solid is pure D. For an original composition **P** this occurs when the liquid reaches the point z , fixed by the line DP , the liquid having traveled on the curve from y to z . At z the liquid, now saturated with D alone, leaves the curve and crosses the D field on the crystallization path fixed by DP , until it reaches one of the curves hQ_2 or Q_1Q_2 , in the present case Q_1Q_2 ; the drying-up point is then Q_2 .

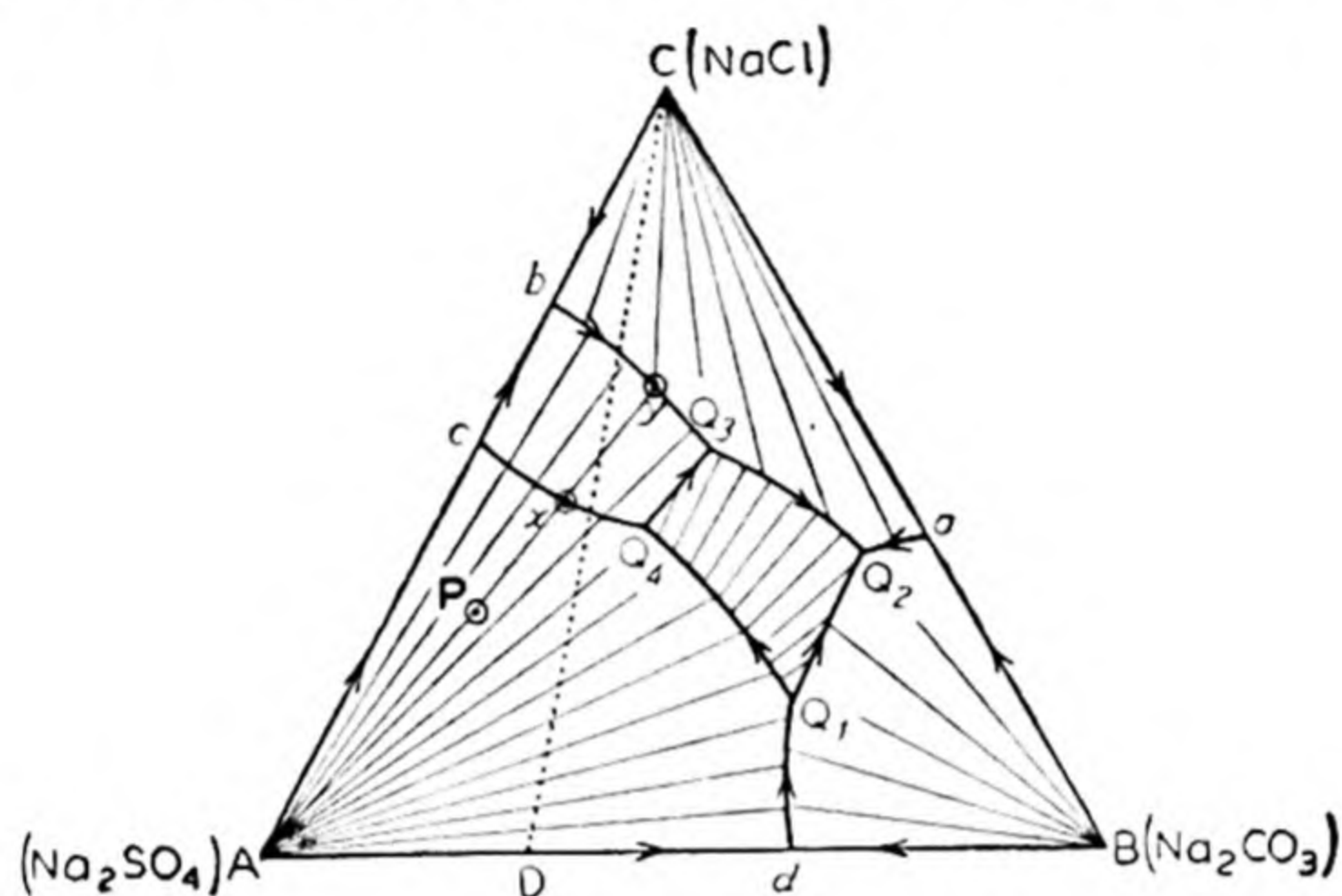


FIG. 16-35. System $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$, at 20° .

At 20° (Fig. 16-35), below a ternary transition point of the type of Fig. 13-17(a), the double salt D is no longer a stable saturating phase in the ternary system, but it still appears in the quaternary system; Fig. 16-35 is the analog of Fig. 12-45(c). The disappearance of the double salt D from the solubility relations of the ternary system is marked by the merging of points f and h of Fig. 16-34, leading to Fig. 16-35, in which the D field (burkeite) is now entirely enclosed within the diagram, as $Q_1Q_2Q_3Q_4$. At the same time there have been other changes: the field BaQ_2Q_1d now represents saturation with $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, CbQ_3Q_2a with anhydrous NaCl as before, and AdQ_1Q_4c with the hydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, while the field bcQ_4Q_3 is the remnant of the field of saturation with anhydrous Na_2SO_4 . In every field the crystallization paths radiate from the salt composition of the solid phase, however, regardless of hydration, so that in both of the two fields last mentioned they radiate from the corner A.

All quaternary solutions must dry up at this temperature either to $A + C + D$ or to $C + D + B$. Hence only the point Q_2 is congruently saturated with its three salts (C, D, and B); the other three invariants are incongruently saturated. But furthermore, for these three points, only the salts saturating Q_3 form a triangle (ACD), and hence while Q_3 is the incon-

gruent drying-up point for solutions in this part (ACD) of the diagram, the points Q_1 and Q_4 are never drying-up points but always purely transition points. (The solids for Q_1 are A, D, and B and those for Q_4 are anhydrous A, hydrated A, and D; and no quaternary liquid, containing NaCl, can dry up to such mixtures.) As for the reaction on each curve and the direction taken by the liquid on it during isothermal evaporation, six curves are "even," with positive crystallization of both salts: dQ_1 , aQ_2 , bQ_3 , Q_3Q_2 , Q_4Q_3 and Q_1Q_2 , so that the directions of falling W_l are as indicated by the arrows. Q_1Q_4 is "odd," with A —, D +. The curve cQ_4 is special, and will be discussed under "dehydration curves"; it has no arrow on it because liquid does not move along it.

Ignoring this curve for the moment, we may discuss the isothermal evaporation of the system, with Fig. 12-45(c) in mind as the temperature analog. The point Q_3 is reached by compositions in the region ACQ_3D , along bQ_3 carrying Na_2SO_4 and NaCl, and along Q_4Q_3 carrying Na_2SO_4 and D. If the liquid started from the triangle ACD, it dries up at Q_3 to leave $\text{Na}_2\text{SO}_4 + \text{NaCl} + \text{D}$ in the invariant, diagonal type of reaction,

$\text{L} + \text{Na}_2\text{SO}_4 \rightarrow \text{NaCl} + \text{D} + \text{H}_2\text{O}$.[↗] Otherwise the Na_2SO_4 is consumed and L travels on Q_3Q_2 to Q_2 to leave $\text{NaCl} + \text{D} + \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. Point Q_2 must be reached by all compositions in DCB. The point Q_1 is reached by compositions in the triangle AQ_1B , on curve dQ_1 , carrying $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The invariant reaction at Q_1 is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} +$

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \rightarrow \text{D} + \text{H}_2\text{O}$,[↗] in the presence of the liquid (Q_1). During the process the liquid is invariant not only in composition but also in its actual quantity, inasmuch as the component C (NaCl) is present only in the liquid, and is not involved in the phase change, which is effectively of lower order. This reaction is therefore entirely analogous to that of the ternary system of Fig. 13-16(a) at the points b or d in isothermal evaporation. During the invariant reaction at Q_1 , solutions from ADQ_1 lose the solid $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and travel away on curve Q_1Q_4 , while those from DQ_1B lose the solid $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and leave on curve Q_1Q_2 . The transition curve Q_1Q_4 is reached, directly or indirectly, therefore, by all liquids with original composition in AQ_1Q_4D . Those starting from DQ_4Q_1 cross the curve without reaching Q_4 and travel across the D field to one of its three other boundaries, finally reaching Q_2 . The others reach point Q_4 , where they remain invariant while the hydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is dehydrated to Na_2SO_4 , and then travel to Q_3 on the curve Q_4Q_3 .

With further change of T the field of a double salt, such as that in Fig. 16-35, may disappear altogether. This disappearance (or appearance) may occur with either rising or falling T , and the course of the change may be

marked by a number of condensed invariant points, of equilibrium of solution + four solids (+ vapor). The field of the double salt in Fig. 16-35 has four boundaries. One of these will disappear at one transition point and the remaining triangular field at a second (Fig. 16-36). Thus the points Q' (at T_2) and Q'' (at T_4) of Fig. 16-36 are both condensed invariant points

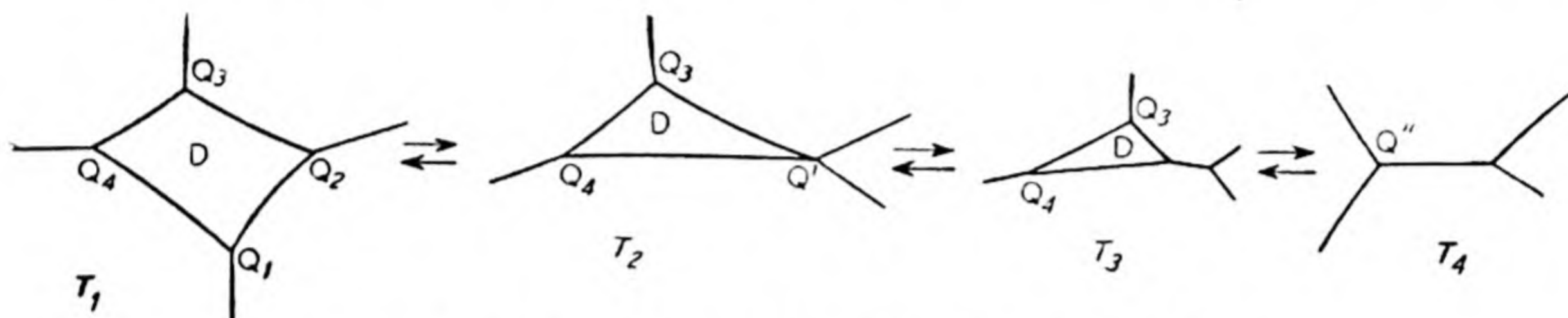


FIG. 16-36. Invariant points involving double salt.

The appearance or disappearance of each new boundary on the field of the double salt marks such an invariant transition point. For the determination of these points, the general method of determining the intersections of condensed univariant equilibria, mentioned in Chapter XIII for ternary systems, is extended, as used by van't Hoff, by Jänecke and by D'Ans. The compositions of univariant solutions Q_1 and Q_2 (Fig. 16-36), for example, each saturated with three solids, two of them common to both solutions, are plotted against the temperature. The plot of the concentration of any one salt, against T , gives, at the intersection of the two curves, the temperature of the transition and the concentration of that salt at the transition point. For the full composition (three independent composition variables), the procedure may be repeated for two other concentrations, against T .

One more example of a Jänecke diagram will be discussed, that for the system $\text{FeSO}_4\text{--Li}_2\text{SO}_4\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ at 30° (Fig. 16-37).¹¹ Clockwise, the fields are for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ($=A$), $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ($=C$), $\text{Li}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ ($=D_2$), $(\text{NH}_4)_2\text{SO}_4$ ($=B$) and $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ($=D_1$, Mohr's salt). The double salts are both congruently soluble in water; hence the crystallization paths radiate from the points D_1 and D_2 lying on the ternary boundaries of their respective fields. In this projection the largest field (generally that of the least soluble salt) is that of D_1 ; the smallest is that of $(\text{NH}_4)_2\text{SO}_4$, the most soluble. The curves Q_1Q_2 and Q_2Q_3 are solutions saturated with the pairs $D_1 + D_2$ and $D_1 + C$, respectively. Each of these curves is cut by the line connecting its saturating salts; hence the points m_1 and m_2 are congruently saturated solutions, saddle points of maximum "water content" on their curves. This suffices to fix the directions of isothermal evaporation on all curves, and to establish that all three invariants are congruently drying-up points for compositions falling in the

¹¹ F. A. H. Schreinemakers, *Z. phys. Chem.*, **71**, 109 (1910).

triangles defined by their respective salts. The course of isothermal evaporation of any quaternary solution then follows simply from the diagram. It is to be noted that it is possible to prepare a solution saturated with D_1 and any one of the other four solids.

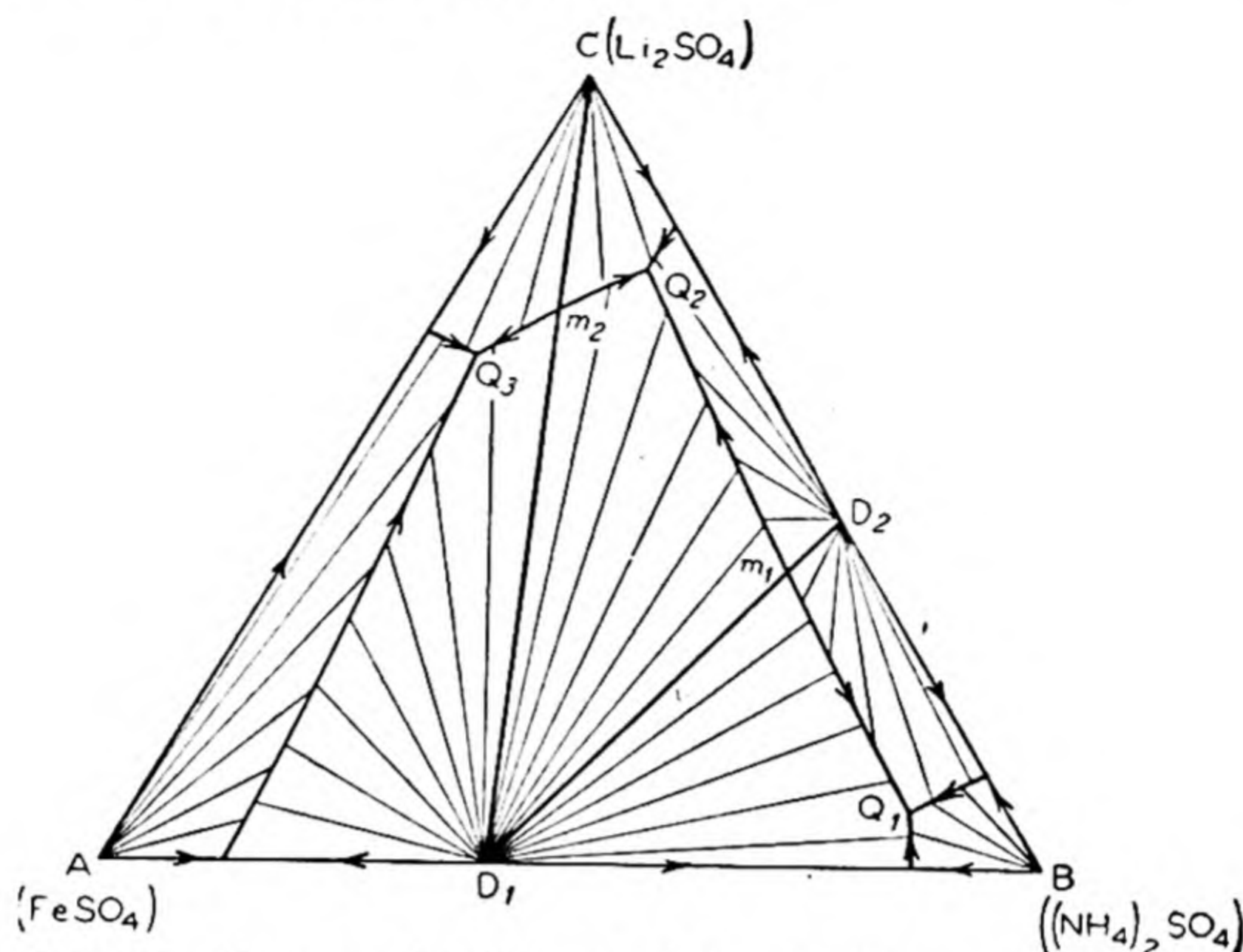


FIG. 16-37. System $\text{FeSO}_4\text{--Li}_2\text{SO}_4\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$, at 30° .

With two such double salts in the system there are two possible arrangements for the isotherm, as in Fig. 16-38. The situation is analogous to the ternary case of Fig. 12-32. Again a single experiment, in the fashion of Guertler's *Klärkreuzverfahren*, should suffice to distinguish the two varia-

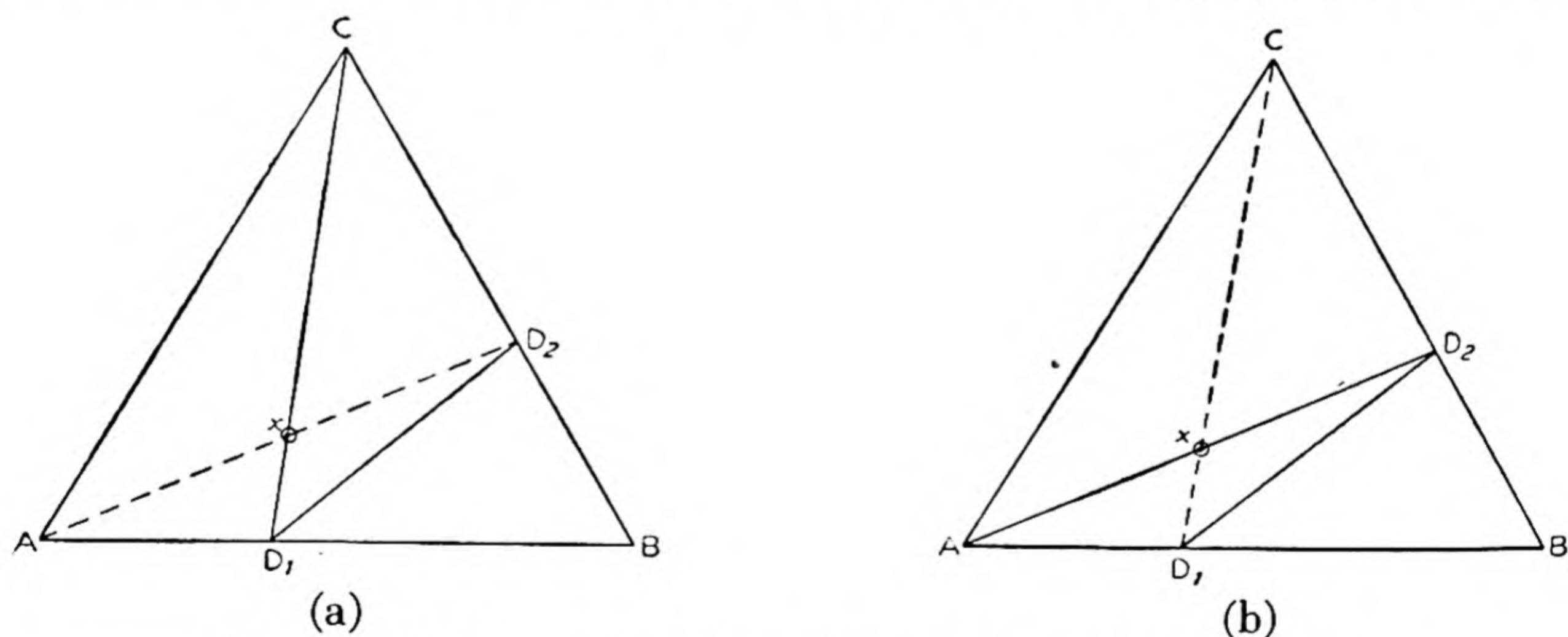


FIG. 16-38. Possible arrangements with two double salts.

tions. If a solution with the salt proportions x is evaporated isothermally to complete crystallization, it will leave a mixture of $C + D_1$ in case (a) and $A + D_2$ in case (b). This will easily be so if the section involved is quasi-ternary, as in Fig. 16-37 itself, with the solution m_2 congruently saturated with C and D_1 . Theoretically the experiment should apply even in the ab-

sence of such congruence, if complete equilibrium between liquid and solid phases could be maintained during evaporation, but in practice the results would generally be inconclusive.

E. Dehydration Curves

We return now to consider the curve cQ_4 of Fig. 16-35, representing "quaternary" solution in equilibrium with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Na_2SO_4 , at arbitrarily constant temperature and either in the open air or under its own vapor pressure. If a liquid **P** with original salt proportions in the region AcQ_4 is evaporated under the conditions of the diagram (20°C and in the open, for example), it precipitates the hydrate and travels on a straight line toward the curve cQ_4 , where, at point x , Na_2SO_4 appears, in an equilibrium involving L , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Na_2SO_4 and water vapor, the hydrate disappearing at the expense of the anhydrous salt. Since the only salt involved is sodium sulfate (component A), the composition of the liquid must remain, during this reaction, on the straight line fixed by the points A and **P** and on the curve of twofold saturation, cQ_4 , or at x . Such a liquid then never travels along this curve; it merely stops on it, with isothermal invariance, until the hydrate is completely transformed to the anhydrous salt. Then it leaves the curve, on the same straight line through A and **P**, until it reaches the curve bQ_3 at y , to proceed subsequently to Q_3 . The liquid is moreover "inevaporable," constant in actual quantity, during the dehydration of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, since the salts NaCl and Na_2CO_3 are not involved in the reaction. This, at least, is the case if only water is volatile, all the other substances being non-volatile. At constant T , moreover, the partial pressure or, more generally, the activity of the water at point x , and in fact anywhere on the curve cQ_4 , must be constant and the same as that in the binary system $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ (vapor) at the same temperature. (The same relation has already been noted for point y of the ternary isotherm of Fig. 12-38(b), and for points b and d of Fig. 13-16(a), which correspond to point c of the present case.

But the isothermal invariance of the solution on the curve cQ_4 during isothermal evaporation requires that the system be (effectively) ternary and not quaternary. At constant T , $F = \alpha - \beta + 1$, and since $F = 0$ and $\beta = 4$ ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Na_2SO_4 , liquid, and vapor), α must = 3. In respect to the process of isothermal evaporation along the curve cQ_4 (to be called a "dehydration curve"), therefore, the system must be considered ternary if the only reaction involved is this dehydration, regardless of the actual number of non-volatile substances present in the liquid phase. The invariance of the system on this curve is otherwise not explainable.

This is then an example of what was said in Chapter I: that the order

(number of components) of a system is not an inherent property of the system, but that it is merely a certain term required for the description of the equilibrium state under observation from the point of view of the Phase Rule.

The analog of the isopiestic dehydration curve cQ_4 in the polyhydric projection of Fig. 16-35 is the isothermal curve $t_1t'_1$ in the polythermal projection of Fig. 12-73, for a ternary system involving polymorphism of a pure solid phase. Since only salt ratios are plotted in Fig. 16-35, the difference in hydration of the pure salt Na_2SO_4 corresponds to the difference between the polymorphic forms of the component C in Fig. 12-73. In the equilibrium of curve $t_1t'_1$ of the latter system, the system is effectively binary, since the ratio of A to B is of no significance; a liquid being cooled at constant pressure becomes invariant anywhere on the curve $t_1t'_1$, in a 3-phase equilibrium. We may note that in quaternary isobaric isotherms, curves of polymorphic transition of a pure solid are not to be encountered, since at a particular pressure and temperature only one form of the polymorphic solid is stable, whether or not involved in an equilibrium with a solution of any complexity. Hence the dehydration curve here discussed is the analog and equivalent of the polymorphic transition curve of the ternary polythermal diagram.

F. Solid Solution

If the saturating solid phases form solid solutions, a great number of possibilities arise. But if we recall that the Jänecke polyhydric projection of the condensed isotherm of the quaternary aqueous salt system is schematically identical with the polythermal projection of a condensed ternary system, there is essentially nothing new to be brought out. The projected isotherms will be schematically merely the polytherms of Chapters X-XII for the additive systems. Those polythermal diagrams will here apply with the substitution of W_1 , the water content (strictly the aqueous vapor pressure) of the saturated solution, for the variable of temperature. If, for example, the three salts form ternary solid solution without any miscibility gap, then the isothermal aqueous solubility surface will be single and continuous, and the only question is that of the slant and shape of this surface. Some of the possibilities are therefore those shown in Figs. 10 and 11 of Chapter X. The system $\text{H}_2\text{O}-\text{K}_2\text{SO}_4(\text{A})-\text{K}_2\text{CrO}_4(\text{B})-\text{K}_2\text{MoO}_4(\text{C})$, with apparently unlimited solid solubility of the three salts, would illustrate, at room temperature, Fig. 10-10(b).¹² With complete equilibrium maintained between liquid and solid phases, any quaternary liquid in this system

¹² E. Jänecke, *Z. Elektrochem.*, **43**, 924 (1937).

would dry up to a ternary solid. But if complete equilibrium is not maintained, or if the solid is "effectively removed" during evaporation, then the course followed by the liquid is given by the arrows of the diagram, which indicate the direction of falling W_l . The W_l maximum is at A since K_2SO_4 is the least soluble salt, and the minimum is at C, the drying-up point, since K_2MoO_4 is the most soluble salt.

If there is a solid miscibility gap bordering on one pair of salts alone, the diagram would be of the type of Figs. 49, 52, 55, and 60 of Chapter XI. If the solid MG runs from one to another pair of salts, the isotherm appears as in Figs. 6, 9, 10, 13, 16, 17, 19, 20 of Chapter XI. In this case, if one of the salts is pure and the other solid phase is binary, we have Figs. 12-5 and 12-6, with straight line crystallization paths for the field of saturation with a pure salt. The system H_2O -RbCl (A)- NH_4Cl (B)-KCl (C) at room temperature would appear as in Fig. 11-6,¹² with the MG in the ternary solid solution running from the KCl- NH_4Cl to the RbCl- NH_4Cl side, and with that direction for falling W_l . If the solid immiscibility is such as to give rise to liquid of threefold saturation, the result will be diagrams like Figs. 21, 29, 32, 35, and 40 of Chapter XI and Figs. 9 and 11 of Chapter XII. A point there labeled "E" now represents a solution congruently saturated with its three salts, or a drying-up point of minimum W_l ; the points marked "P" are now isothermally invariant transition points, and may be incongruent drying-up points.

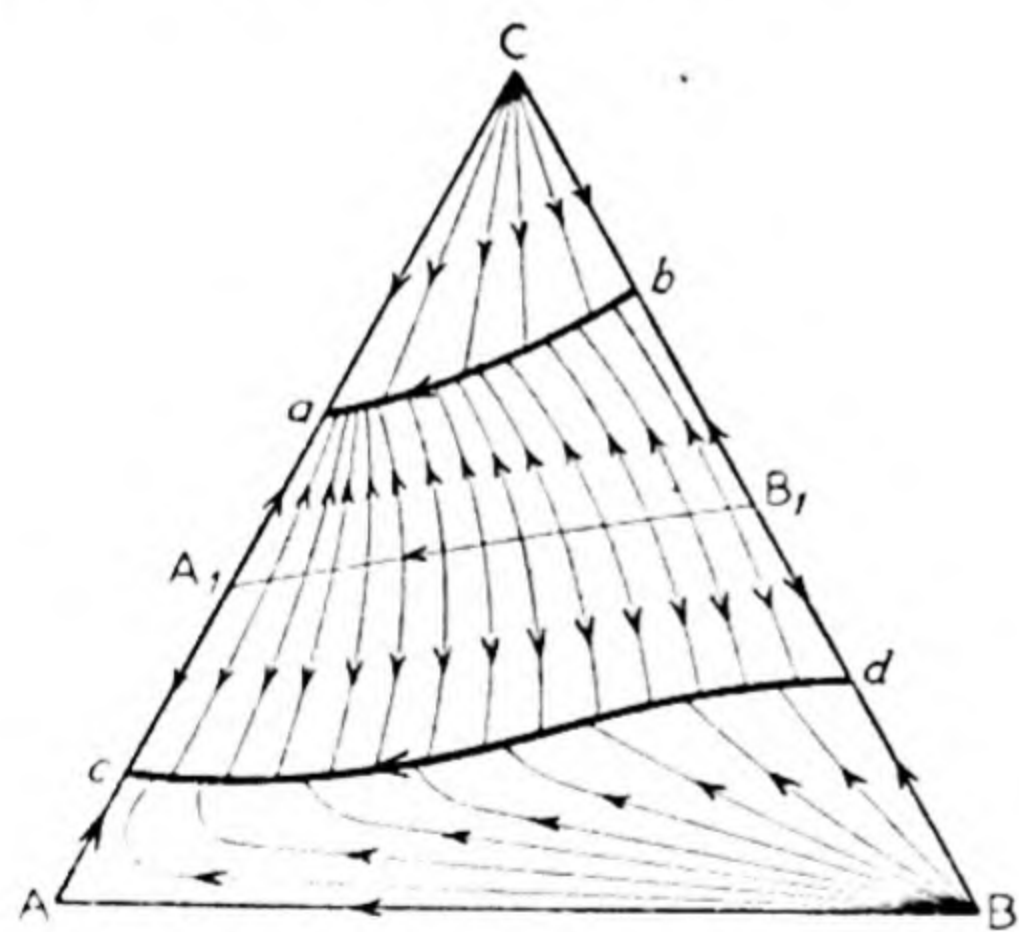


FIG. 16-39. Solid solution of congruently soluble double salts.

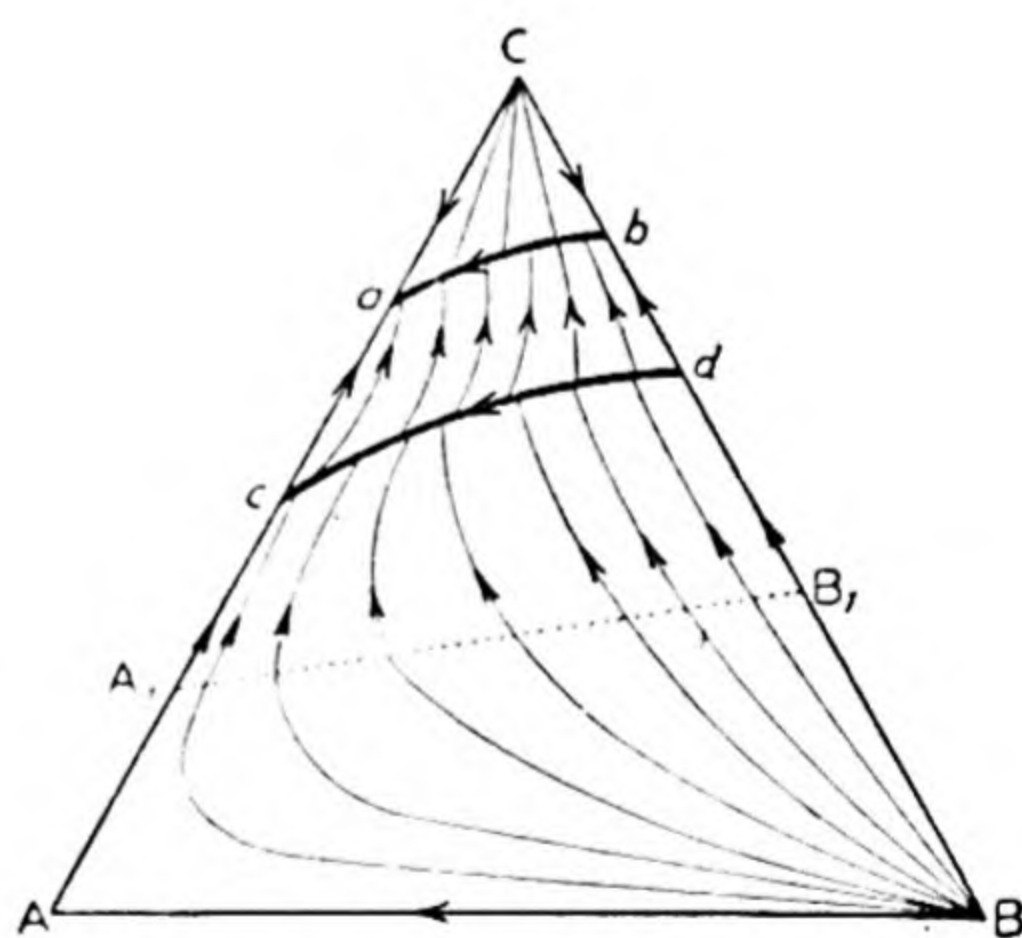


FIG. 16-40. Solid solution of incongruently soluble double salts.

If solid solution between double salts is involved, the projected isotherms would resemble the polythermal projections of Figs. 47, 50, 51, 52, 56, 59, and 62, chapter XII. Thus, if there is continuous solid solution both between the salts A and B and between the corresponding double salts A_1 (such as AC) and B_1 (or BC), there will be two liquid curves of twofold saturation, but no invariant point; schematic isotherms are shown in Figs. 16-39 and

16-40. The line A_1B_1 now represents the continuous solid solution of the compounds, whether hydrated or not, as always. If these compounds are both congruently soluble, the relations are those in Fig. 16-39. The upper curve ab is liquid saturated with C and the solid solution of the compounds; the lower curve cd is liquid saturated with two solid solutions, one of the compounds, on the line A_1B_1 , the other of the simple salts A and B, on the line AB. In this case the line A_1B_1 also represents quaternary liquid solutions joining the ternary liquid solutions A_1 and B_1 each congruently saturated with respect to one of the double salts, and hence also a ridge of maximum "water content" on the solubility surface ($abdc$) of the compound solid solution. The system $H_2O-CuSO_4-(NH_4)_2SO_4-K_2SO_4$ at 25° is an example of Fig. 16-39, with $A = (NH_4)_2SO_4$, $B = K_2SO_4$, $C = CuSO_4 \cdot 5H_2O$, $A_1 = (NH_4)_2SO_4 \cdot CuSO_4 \cdot 6H_2O$, $B_1 = K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$.¹³ If both compounds are incongruently soluble, both of the curves for liquid of twofold saturation will lie on one side of the line A_1B_1 , as in Fig. 16-40.

The ternary analog (with T as the variable in place of W_l) for Fig. 16-39 is Fig. 12-47(a); for Fig. 16-40 it is Fig. 12-56(a).

The system $H_2O-(NH_4)_2SO_4$ (A)- K_2SO_4 (B)- $MgSO_4 \cdot 7H_2O$ (C) at 30° ¹⁴ is similar to the $CuSO_4$ system just mentioned, with the difference that whereas A_1 , or $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$, is congruently soluble, B_1 , or $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$, is not. Hence the curve cd crosses the line A_1B_1 , c being below it, d above it.

G. Two Liquid Phases

Fig. 16-41 is the 25° isotherm (schematic) of the system of the liquids chloroform (A)-water (B)-acetic acid (C)-acetone (D).¹⁵ The only pair with limited miscibility is A-B; the faces ABC and ABD of this tetrahedron are schematically represented by Fig. 10-13. There is now a binodal region of conjugate quaternary liquids given by points on the binodal surface, one on each side of the consolute or critical solution curve KK' . In the system of Fig. 16-42, the schematic isotherm (at $20^\circ F$) of the system naphtha (A)-furfural (B)-isobutene (C)-butadiene (D),¹⁶ the pairs AB and BC both have limited miscibility, and a binodal region of the general shape of a tunnel runs from the ABD to the BCD face. The ends of the consolute curve KK' lie on these faces. In this 2-liquid region the conjugate liquids have compositions on the binodal surface, again one on each side of the consolute curve.

¹³ R. Hayami, *Mem. Col. Sci., Kyoto Imp. Univ.*, **4**, 359 (1921).

¹⁴ A. Weston, *J. Chem. Soc.*, **121**, 1223 (1922).

¹⁵ A. V. Brancker, T. G. Hunter and A. W. Nash, *J. Phys. Chem.*, **44**, 683 (1940).

¹⁶ A. S. Smith and T. B. Braun, *Ind. Eng. Chem.*, **37**, 1047 (1945).

Fig. 16-43 involves an example in which the liquid immiscibility is caused by the dissolving of salts. Fig. 16-43(b) is the schematic 30° isotherm of the system alcohol (A)– Li_2SO_4 (B)– $(\text{NH}_4)_2\text{SO}_4$ (C)–water (W), studied by Schreinemakers² over a range of temperature. The system

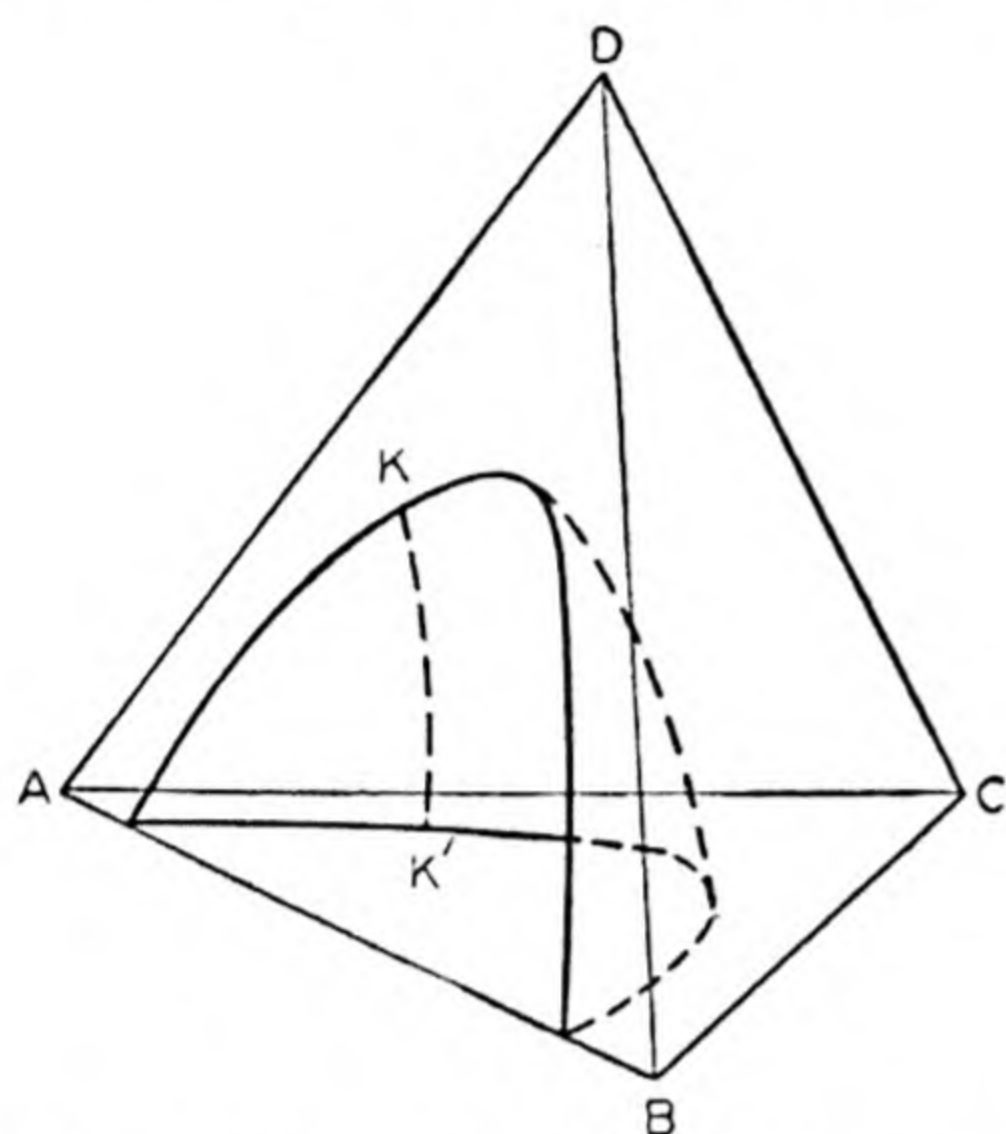


FIG. 16-41. Liquid *MG* in one binary system only.

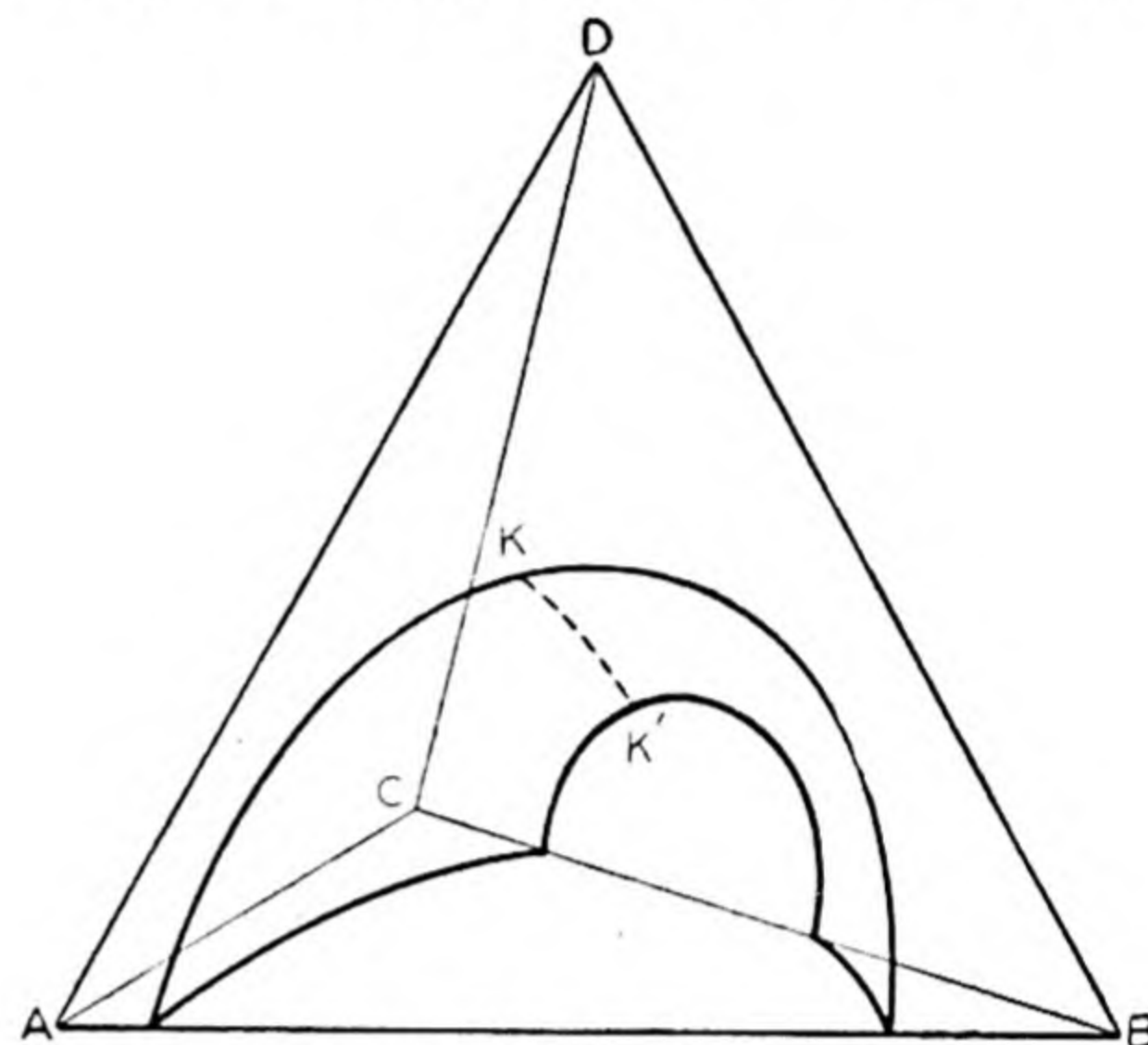
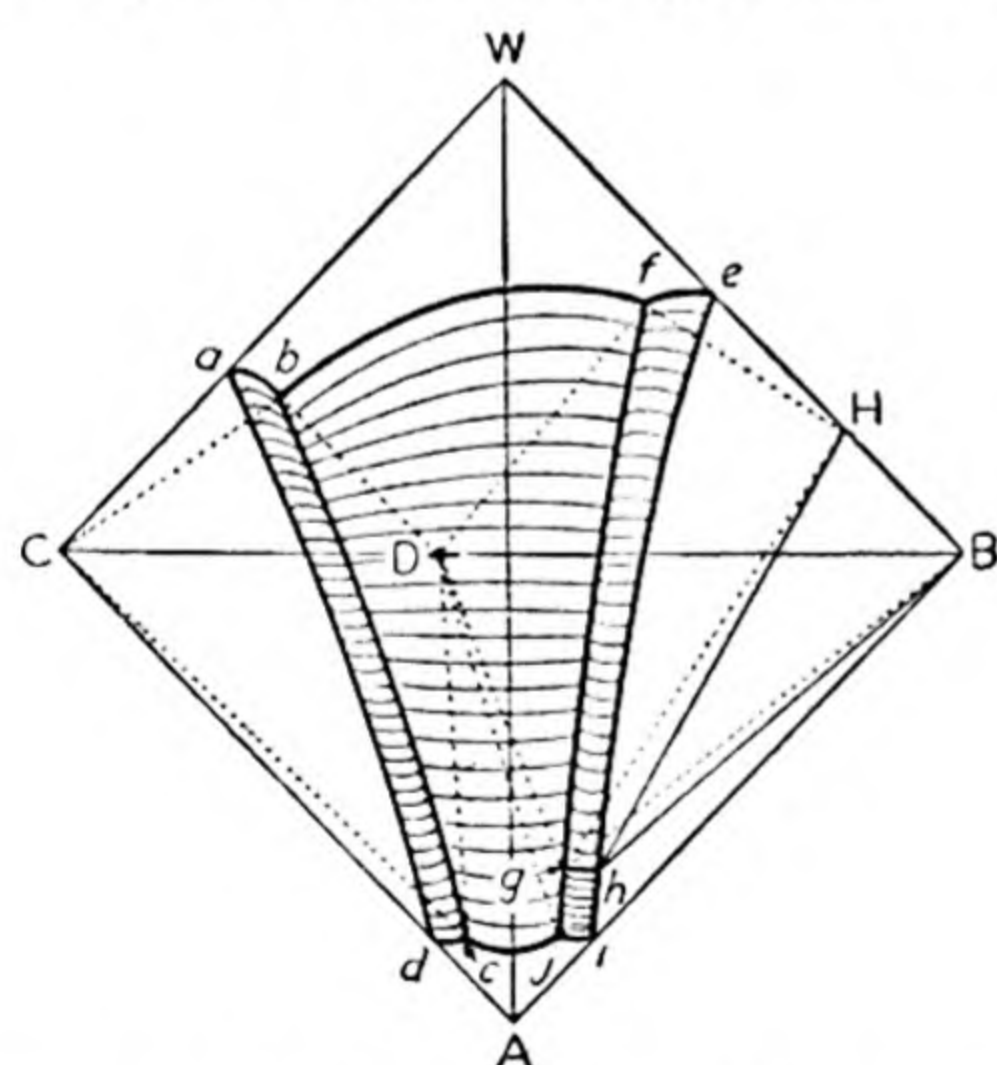
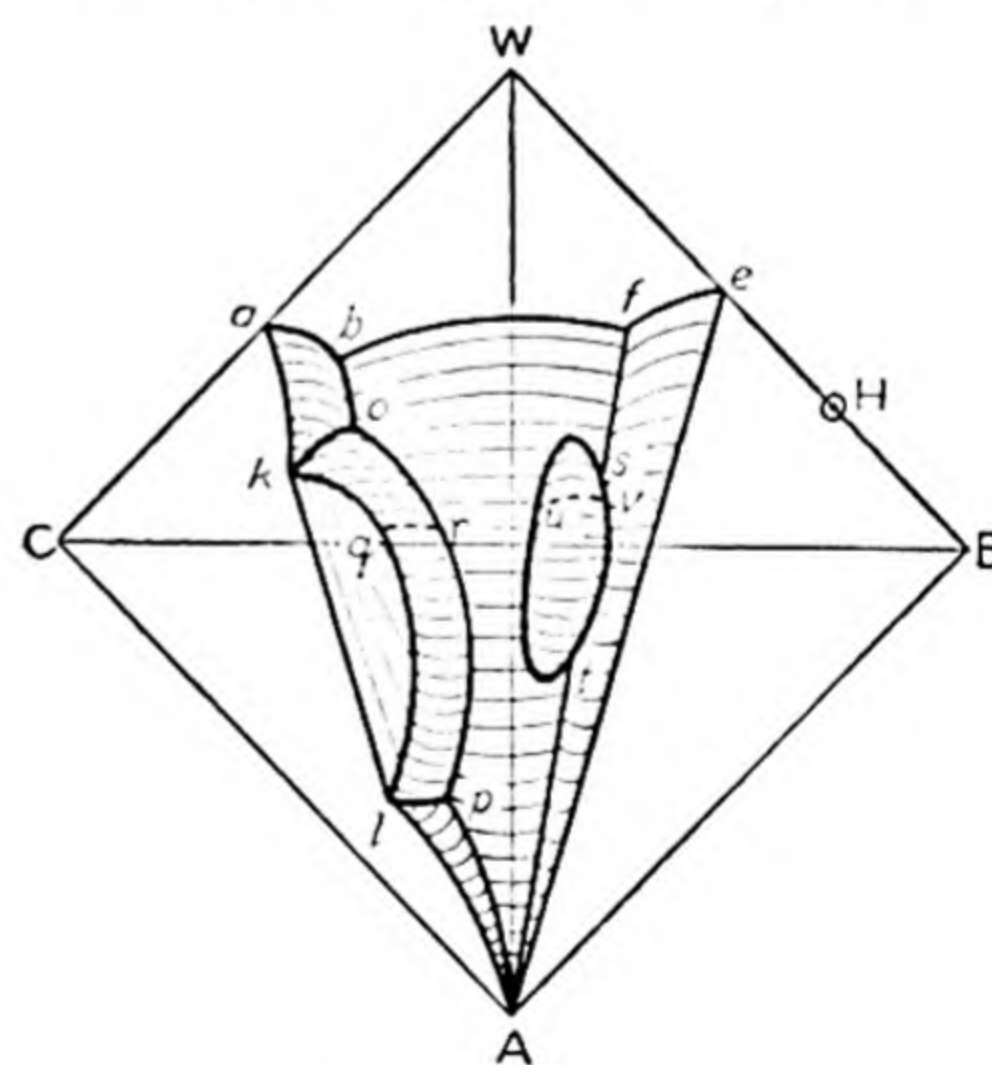


FIG. 16-42. Liquid *MG* involving two binary systems.

Li_2SO_4 – $(\text{NH}_4)_2\text{SO}_4$ – H_2O appears as part of the quaternary system of Fig. 16-37, with the solid phases $(\text{NH}_4)_2\text{SO}_4$, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (or H) and a congruently soluble double salt, $\text{Li}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ (or D). If the liquid did not develop a miscibility gap on addition of alcohol, the quaternary isotherm



(a) explanatory, assuming single liquid phase.



(b) actual (schematic), with miscibility gaps.

FIG. 16-43. System alcohol(A)– Li_2SO_4 (B)– $(\text{NH}_4)_2\text{SO}_4$ (C)–water(W), at 30°.

might look like Fig. 16-43(a). In this diagram the tetrahedron is viewed from the water–alcohol edge (WA). The line WA represents a binary liquid, and the saturation surfaces are therefore being viewed from the side of unsaturated liquid, in the manner of a “square orthogonal” projection.

It is assumed, for simplicity, that the double salt remains congruently soluble in alcohol. The surface $abcd$ is that for saturation with $(\text{NH}_4)_2\text{SO}_4$, and tie-lines from it are confined in a space converging to the point C. A similar surface, $efgh$, represents solution saturated with $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, with tie-lines confined in a space converging at H. Near the alcohol corner this surface is assumed to be replaced by one for anhydrous Li_2SO_4 , $ghij$, with tie-lines converging at the corner B. Actually all the points $dcghij$ are so close to the A corner that they are experimentally not distinguishable from point A, and they are so shown in Fig. 16-43(b). The surface $bfgjc$ represents solution saturated with the double salt D, which lies on the line CB, as seen in the figure through its solubility surface. Fig. 16-43(a) is not the actual system, but serves as basis for understanding the relations in Fig. 16-43(b) (also schematic, except for the corner A).

The system $(\text{NH}_4)_2\text{SO}_4$ -water-alcohol at 30° is of the type of Fig. 14-1. The ternary solubility curve ad of Fig. 16-43(a) is interrupted by a binodal curve, and points k and l are the conjugate liquids saturated with C, or $(\text{NH}_4)_2\text{SO}_4$; q is the plait point of the ternary isotherm. The binodal curve then extends into the quaternary tetrahedron and its surface is viewed, as $kopl$, from the side of homogeneous liquid. Quaternary liquids on the curves ko and lp , lying as they do on the saturation surface of C, are conjugate and saturated with C. Between the ternary curve kql and the quaternary curve orp the quaternary liquids are conjugate, one on one side of qr and one on the other, but not saturated with any solid. The curve qr is the quaternary critical curve. Liquids then on the curve orp are again saturated conjugate liquids, the solid phase however being the double salt D. Point r then is an isothermal plait point for saturated solutions.

There is also a binodal region intersecting the curve fg of Fig. 16-43(a), and hence the surfaces for D and H. This 2-liquid region does not reach the ternary face AWB. The quaternary critical curve is uv . The liquids on the curve sul are conjugate and saturated with D; the conjugate liquids on the curve svl are saturated with H. Points s and l are the two liquids of a 4-phase isothermally invariant equilibrium involving the solids D and H; the liquids o and p similarly are part of an isothermally invariant equilibrium involving the solids C and D.

At lower temperature (6.5°) this second binodal region has disappeared, and the first has drawn away from the ternary face AWC, so that it then looks like $sulv$ of Fig. 16-43(b). At higher temperature (50°) they have merged into one, but still not reaching the ternary face AWB; at this temperature, then, the points r and u have merged, and there is no plait point for saturation with D.

Chapter XVII Quaternary System of Water and Reciprocal Salt Pair

A. Graphical Representation of Isotherm

1. Composition Units

A system made from water and salts, in any proportions, which contain only four radicals or "ions," is a quaternary system, provided there is no effective hydrolysis of any salt. If three of the four radicals are of one sign, we have three simple salts with a "common ion" which, involving no double decomposition either among the salts or between the salts and water, is a quaternary system of the simple or additive type already described. If two of the radicals are of one sign and two of the other, the salts constitute a reciprocal salt pair related by the interaction $AB + CD \rightleftharpoons AD + CB$. The resulting quaternary system, of water + reciprocal salt pair, is here considered separately, because of the special type of graphical representation required. In either case, however, whether additive or reciprocal, the quaternary solution requires only three analytical determinations for the establishment of its composition. These determinations may be the quantities of two of the radicals, A, B, C, and D, and the quantity of water, in a given quantity of sample, or the quantities of three of the radicals, again in a given quantity of sample. Although, in any actual case, more determinations may be deemed desirable for higher accuracy, three are sufficient, and the composition may be calculated therefrom through the following equations: Σ equivalents of positive radicals = Σ equivalents of negative radicals (here $A + C = B + D$); and, weight of water + weights of salts = total weight. The result may then be expressed in various ways for tabulation and plotting, as listed in Table 17-1 for the following hypothetical analytical composition, in weight percentage: 8.4% A, 7.2% C, 60.4% W; or 8.4% A, 7.2% C, 15.0% D. The equivalent weights are assumed to be A:20, B:30, C:40, D:50, W:18.

In each of the methods (a) to (f), with compositions in terms of W and three of the salts of the reciprocal system, there are two combinations in which the composition involves only positive terms, and two in which a negative term is necessary. In method (g) the three salt components are no longer specified, and the composition is expressed in terms of the equiva-

TABLE 17-1. TABULATION OF COMPOSITION DATA

METHOD (a) — <i>Weight percentages of W and Three Salts</i>					
AB	CD	AD	CB	Σ Salts	W
15.0	16.2	8.4	...	39.6	60.4
21.0	27.0	...	— 8.4		
6.0	...	21.0	12.6		
...	— 10.8	29.4	21.0		
METHOD (b) — <i>Equivalents per 100 grams total</i>					
0.30	0.18	0.12	...	0.60	3.36
Etc.					
METHOD (c) — <i>Equivalent percentage</i>					
7.58	4.55	3.03	...	15.15	84.85
Etc.					
METHOD (d) — <i>Grams salt per 100 grams water</i>					
24.8	26.8	13.9	...	65.6	
Etc.					
METHOD (e) — <i>Salt Equivalents per 100 grams water</i>					
0.497	0.298	0.199	...	0.994	
Etc.					
METHOD (f) — <i>Salt Equivalents per 100 moles water</i>					
8.95	5.36	3.58	...	17.89	
METHOD (g) — <i>Salt Proportions (as radical equivalents) and water content</i>					
A	C	B	D	W	
0.7	0.3	0.5	0.5		
or $N_+ = C/(A + C) = 0.3$				{	
$N_- = D/(B + D) = 0.5$					
				1.525 g/g salt	
				100.6 g/equivalent salt	
				5.60 mole/equivalent salt	
				84.85 equivalent percentage	
				60.4 weight percentage	

lent proportion of the two positive radicals, the equivalent proportion of the two negative radicals, and the water content.

2. Square Pyramid

A complete representation of the isothermal relations of the condensed system is possible in the square pyramid of Fig. 17-1. The base is the square of Figs. 15-1, 3, 5(a) for the salt proportions of the anhydrous reciprocal salt system, with a perpendicular axis rising from its center to indicate the water content. As usual, the reciprocal salts must be plotted in terms of equivalents or of radical proportions, but since the equivalents of water are not interchangeable (reciprocal) with those of the salts, the scale of the water axis is independent of the salt scale. This means that the relation of the height to the dimensions of the square base is arbitrary and chosen according to convenience. In terms of the tabulation of method (c) of

Finally, concerning tie-lines, a mixture of any two compositions lies on the straight line connecting the two points, and the inverse segment ratio gives the ratio not of the weights but of the number of equivalents of the two compositions.

(If the compositions are plotted in terms of method (b) of Table 17-1, equivalents per fixed weight of total, the figure will be an irregular pyramid, the base of which is Fig. 15-5(b), and the height of which represents the number of equivalents of water in 100 g of water. Now the side faces, scalene triangles with non-uniform scales, represent the ternary systems in weight percentage, and the tie-lines in the pyramid involve the weight ratio of the phases.)

The discussion of the projections of Fig. 17-1 and of partial diagrams, is combined, in the next section, with the consideration of the simple case of a system in which the only solid phases are the simple pure salts.

B. Pure Salts as Solid Phases

1. Condensed Isotherm

a. *Pyramidal diagram.* Simple solubility relations, plotted according to Fig. 17-1, then appear as in Fig. 17-2, which is to be compared with Fig. 16-11. The points *a*, *b*, *c*, and *d* represent solubilities of the single salts in

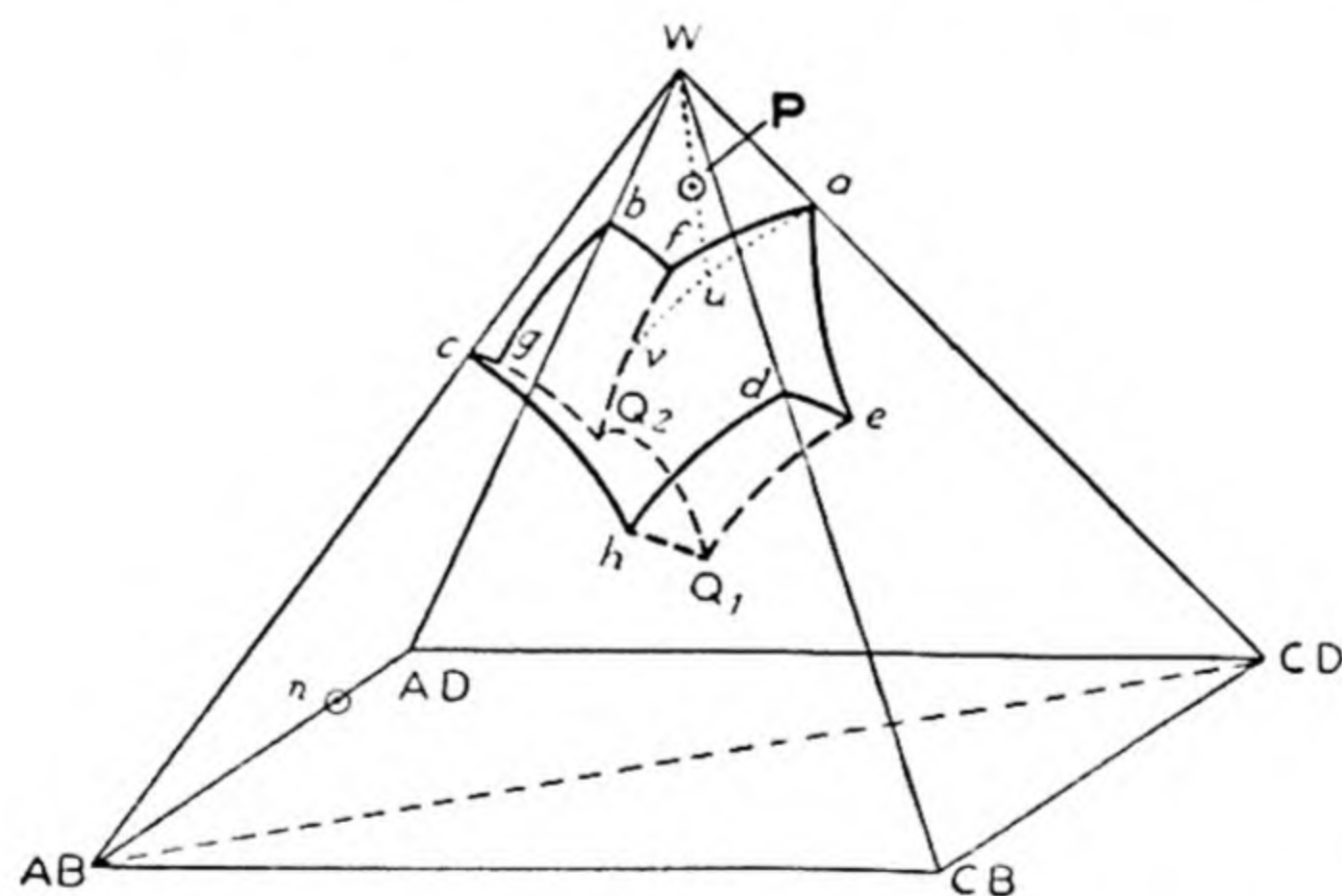


FIG. 17-2. Isotherm for water and reciprocal salts.

pure water, and the surface afQ_2Q_1e represents the surface of saturation with respect to CD. There are four such surfaces, one for each salt. The curves eQ_1 , fQ_2 , gQ_2 , and hQ_1 are solutions of twofold saturation for the pairs $CB + CD$, $CD + AD$, $AD + AB$, and $AB + CB$, respectively. These curves intersect to give two points, Q_1 and Q_2 , of isothermal invariance, for liquid + three solids, in such a way that the solubility surfaces of only one pair of reciprocal salts meet each other; in Fig. 17-2 this occurs on the curve

Q_1Q_2 for liquids saturated with the pair $AB + CD$. Each surface is connected by tie-lines to a single salt, giving spaces of the general form of Fig. 16-12(a); the 3-phase triangles of the five curves describe spaces of the form of Fig. 16-12(b); and there are two isothermally invariant spaces of the form of Fig. 16-12(c), one with Q_1 as the apex and the triangle $AB-CD-CB$ as the base, the other from Q_2 to the triangle $AB-CD-AD$. The interrelation of some of these spaces is seen in Fig. 17-3, a plane section through the pyramid of Fig. 17-2. This section is a plane fixed by the point P , an

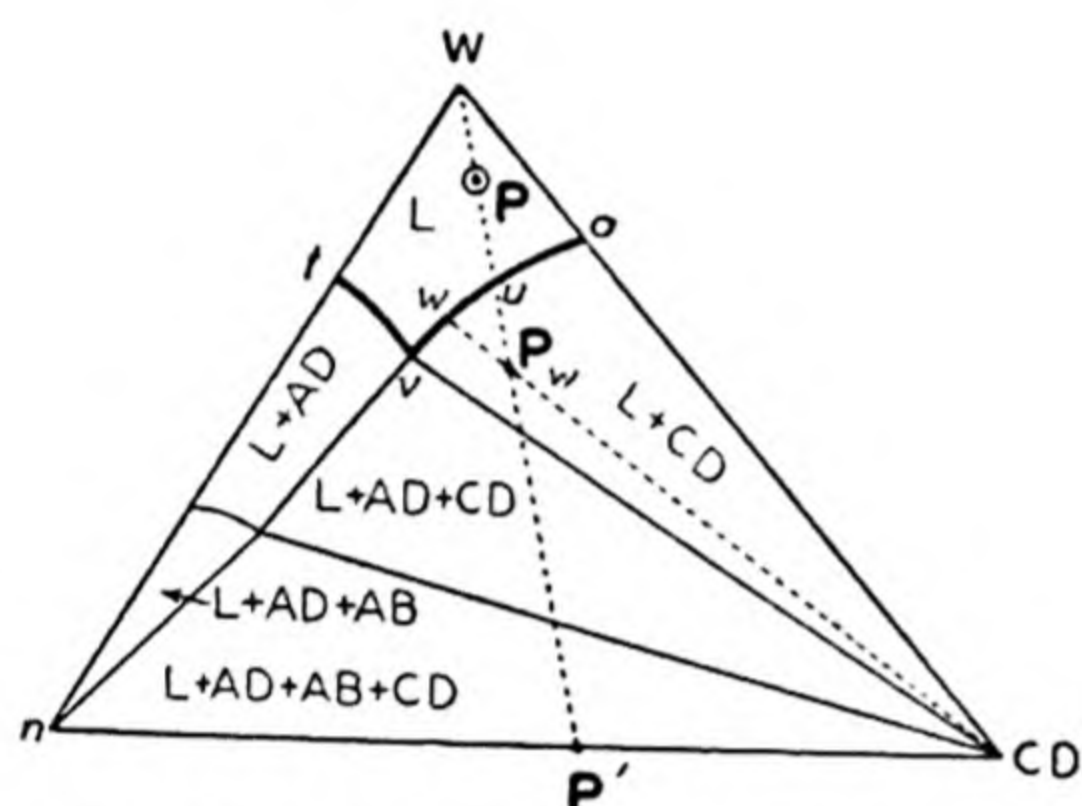


FIG. 17-3. Section of Fig. 17-2.

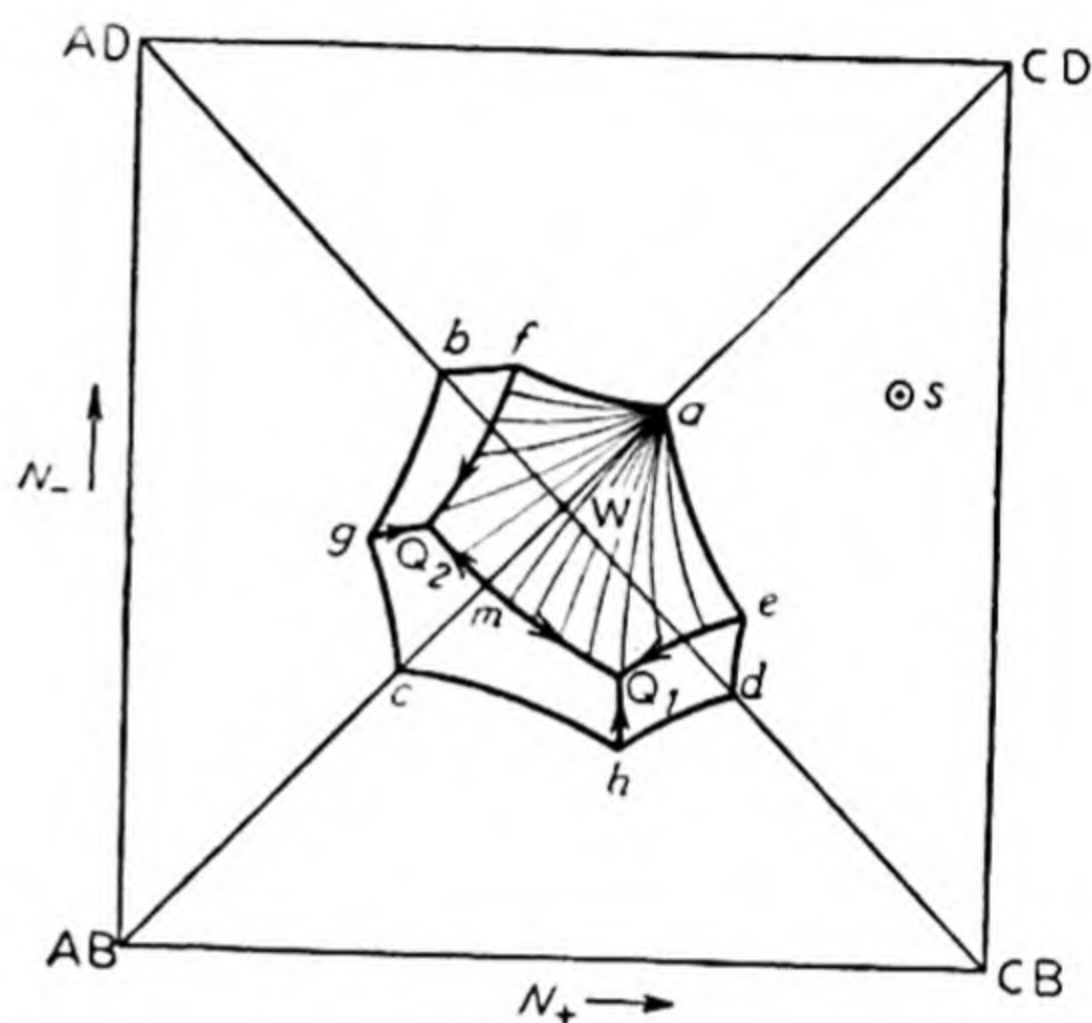


FIG. 17-4. Orthogonal base projection of Fig. 17-2.

unsaturated solution, and the edge $W-CD$; it includes, therefore, the point a , and it intersects the CD surface along the curve auv , the curve fQ_2 at v , and finally the AD surface on a course from v to some point on the ternary curve bg , labeled t on Fig. 17-3; the section intersects the base on the line $CD-n$.

The general process of isothermal evaporation is very similar to that described for Fig. 16-11. All liquids with original composition in the tetrahedron $W-AB-CD-CB$ dry up to a mixture of these three salts and therefore dry up invariantly at point Q_1 ; those in the other tetrahedron must dry up invariantly at Q_2 to leave $AB + CD + AD$. At the temperature (and pressure) of this isotherm, then, the mixture $AD + CB$ is not stable, either in equilibrium with solution or in the dry state. Finally, one of the two invariant points must be congruently saturated with its three salts (the point Q , that is, having a position within the tetrahedron corresponding to its three salts and water), but not necessarily both.

b. *Projections (of Fig. 17-2).* In Fig. 17-4 the curves and points of Fig. 17-2 are projected orthogonally on the base of the pyramid. This projection is plotted directly in terms of method (c) of Table 17-1. The quantity, $\%CD - \%AB$, which we shall call X , is measured on $W-CD$, toward CD ,

and from the resulting point $\%AD$ (or Y) is measured toward AD , parallel to $W-AD$; the quantities X and Y may be positive or negative. Fig. 17-4 will be called simply "the orthogonal diagram." In Fig. 17-5, which we shall call right plane projections, the isotherm is projected orthogonally on

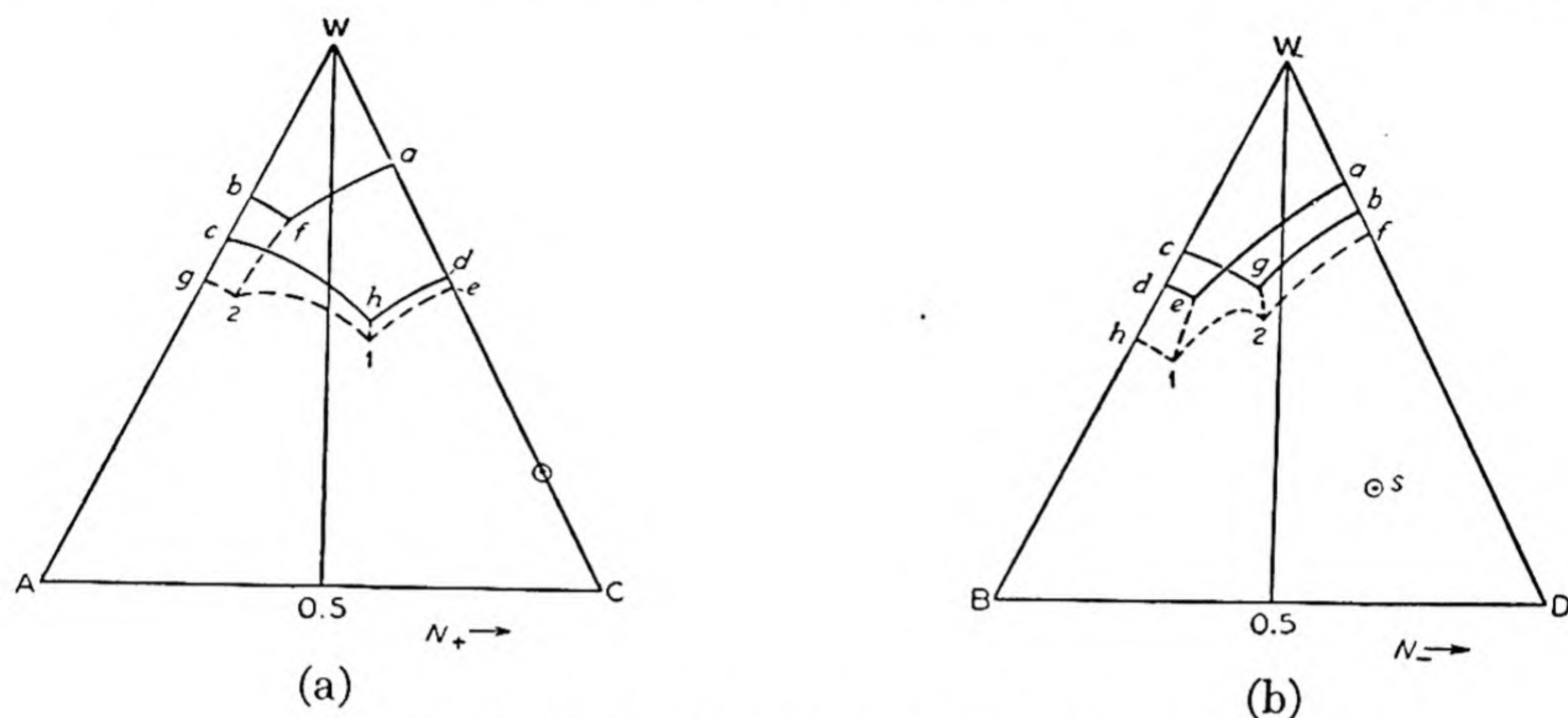


FIG. 17-5. Right plane projections of Fig. 17-2.

vertical planes parallel to the sides of the square: in Fig. 17-5(a) on the plane parallel to $AD-CD$, and in Fig. 17-5(b) on the plane parallel to $AB-AD$. These are plotted by measuring the ion proportions (method (g) of Table 17-1) on the bases, and raising the point toward the water apex in

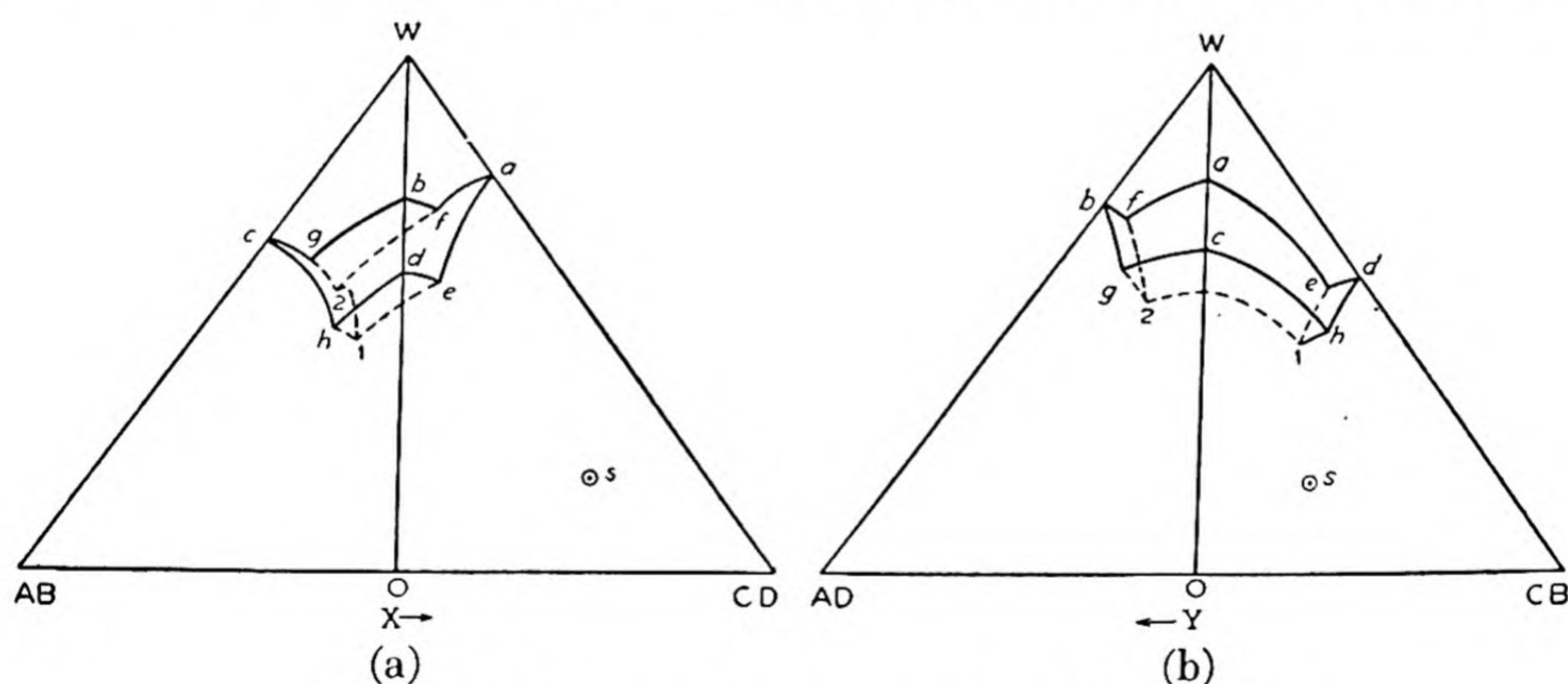


FIG. 17-6. Diagonal plane projections of Fig. 17-2.

proportion to the equivalent percentage of W . In Fig. 17-6, which we shall call diagonal plane projections, the diagram is projected orthogonally on vertical planes parallel to the diagonals of the square: in Fig. 17-6(a) on the plane parallel to $AB-CD$ and in Fig. 17-6(b) on the plane parallel to

AD-CB. In Fig. 17-6(a) the equivalent %W is first measured upward on the altitude, and from the point the quantity X (defined above as %CD - %AB) is measured horizontally toward CD; in Fig. 17-6(b), %W is similarly fixed, and then Y (= %AD) is measured toward AD.

In Fig. 17-7 the diagram is projected radially or perspectively on the base from the W apex. This is the Jänecke diagram, showing salt proportions only, and, of course, it is most readily plotted in terms of the ion proportions as tabulated under method (g) of Table 17-1, with $N_+ = C/(A + C)$ and $N_- = D/(B + D)$. The points P, v , n , l in parenthesis indicate the positions of points involved in Figs. 17-2 and 17-3.

1. *Reading of projections.* Any two projections may contain complete information about a quaternary composition. With Fig. 17-4 and Fig. 17-5(a) or 5(b), for example, the right plane gives %W, the orthogonal gives %AD(=Y) and X ; then %AB = $(100 - \%W - X - Y)/2$. Fig. 17-4 together with Fig. 6(a) or 6(b) would similarly suffice. With Fig. 17-4 and Fig. 17-7, the Jänecke gives the salt proportions; then comparison of the distances of the two points from the center

gives the water content since, as pointed out under Fig. 17-1, $100 PP'/P'W = \%W$. With the salt proportions from the Jänecke diagram, %W may also be read from any one of the four projections of Figs. 17-5 and 17-6, as a second projection. Two right plane projections by themselves similarly give the ion proportions and %W, while two diagonal planes give X , Y and %W, whence the composition may be obtained as above. From a right plane such as Fig. 17-5(b) and a diagonal plane such as Fig. 17-6(a), we have %W, N_- and X directly, whence $N_+ = 1 - N_- + X/(100 - \%W)$ and $Y = (100 - \%W)(2N_- - 1) - X$.

2. *Transformations of projections.* With %W known, an orthogonal (base) diagram may readily be transformed into a Jänecke diagram as explained in Chapter XVI. The ternary points are extended to the sides of the square by straight lines from the center, and the quaternary points (P in the orthogonal diagram) are extended, by the method of parallels, so that $100 PP'/WP' = \%W$, the Jänecke point being P'. The Jänecke diagram may easily be derived from the right plane projection (Fig. 17-5(a)), if the ion proportion N_- , or $D/(B + D)$, is known or, therefore, from a pair of such planes. The same may be done from the diagonal plane projection

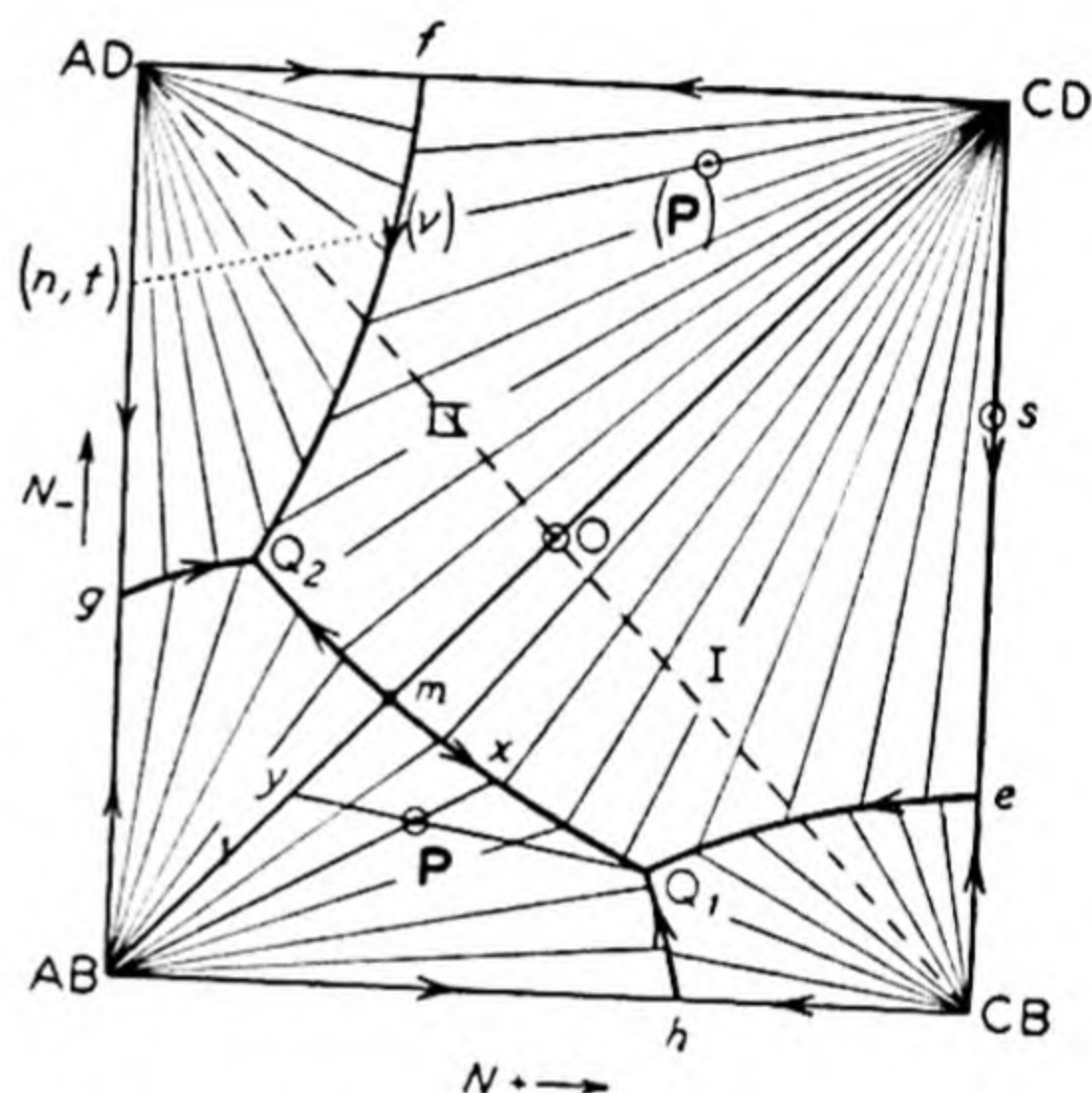


FIG. 17-7. Jänecke diagram of Fig. 17-2.

(Fig. 17-6(a)), if %CD, or Y , is known, or from the pair. Either of the base diagrams (orthogonal or Jänecke) may be transformed to the right plane or diagonal plane projections, as shown in Fig. 17-8, if %W is known. If, as usual, P is the orthogonal and P' the Jänecke point on the base, one of these points may be obtained from the other, with $\%W = 100 \mathbf{PP'}/\mathbf{WP'}$. The lines $P'm$ and $P'd$ are drawn, perpendicular to AD - CD and AB - CD respectively, and then the lines mW_1 and dW_2 . The right plane projection M is then fixed on mW_1 by a line from P perpendicular to AD - CD , and the diagonal plane projection D is fixed on dW_2 by a line from P perpendicular to AB - CD . Fig. 17-8 therefore shows the graphical interrelation of all four types of projections.

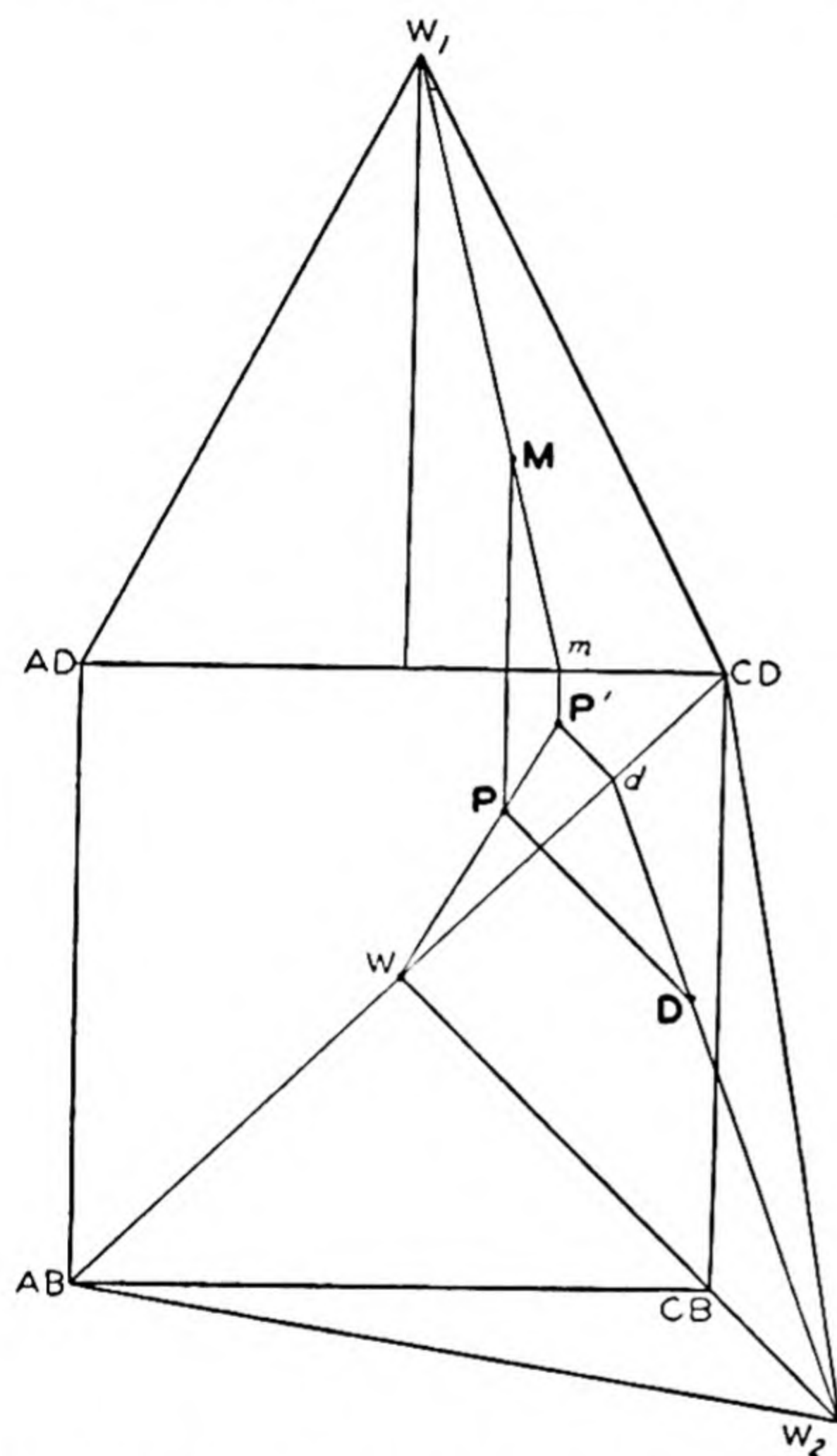


FIG. 17-8. Inter-relation of the four types of projections.

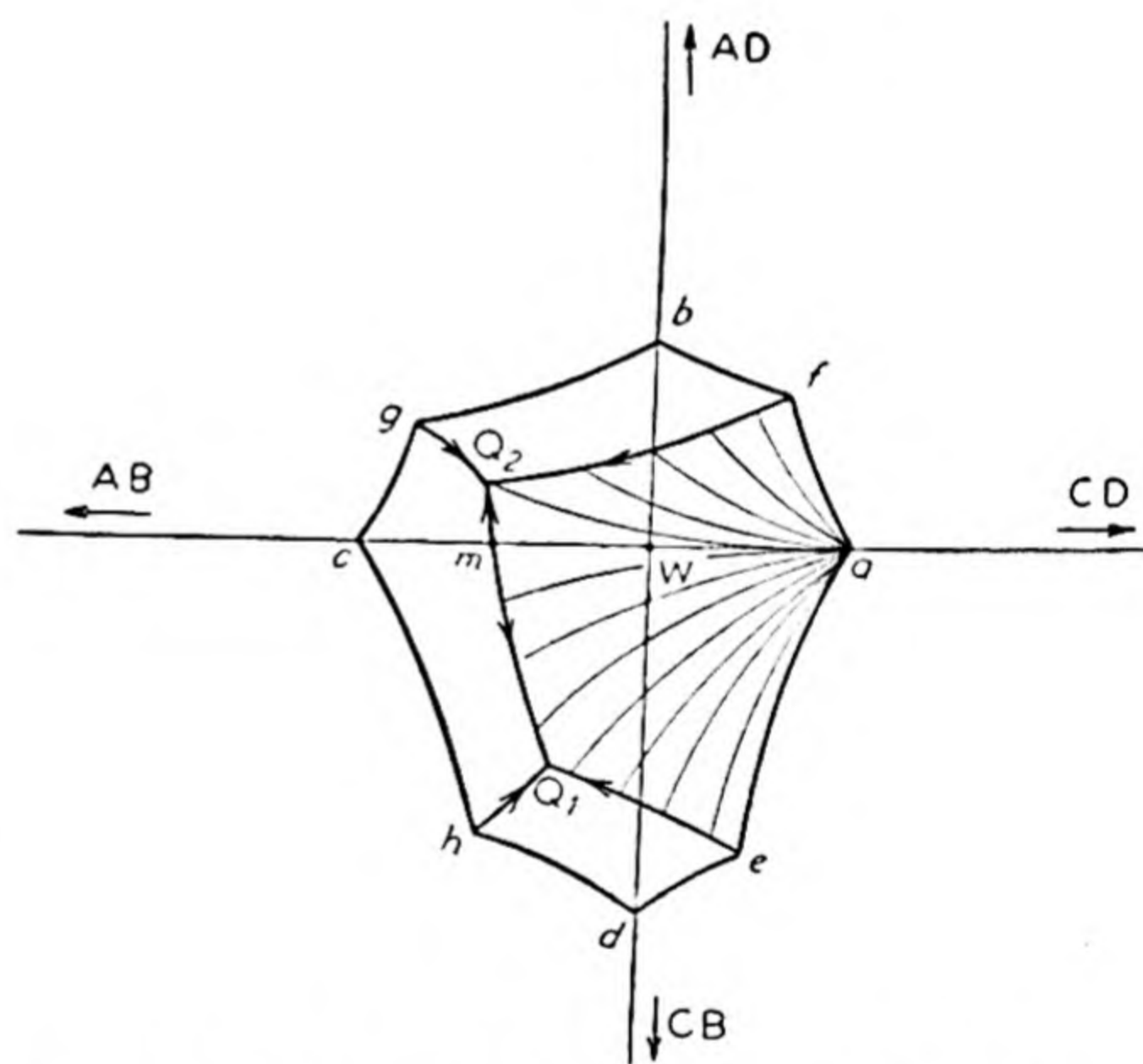


FIG. 17-9. Löwenherz diagram for isotherm of Fig. 17-2.

3. *Tie-lines.* On any of these projections the convergence of tie-lines for the equilibrium of liquid + a single solid may be used for the identification of the solid phase. The composition of the solid phase may be determined by studying the convergence of the tie-lines on a suitably chosen pair of projections. Convergence at the point marked s on the various projections (Figs. 17-4 to 17-7) would, for example, indicate the solid phase to be a hydrated, 2:1 double salt of CD and CB . From Fig. 17-5(a), for example, the solid is seen to contain no A and from Fig. 17-5(b) it is seen to contain D and B in the ratio 2:1; its hydration is read from either of these projec-

tions. Alternatively, the salt proportions may be read directly from Fig. 17-7 as 2CD:1CB, and the hydration directly from any of the projections of Figs. 17-5 and 17-6, or by comparison of the distance W_s in Fig. 17-4 with the distance O_s in Fig. 17-7, since $\%W = 100(O_s - W_s)/O_s$. As usual, the phase ratios, in equivalents, follow from the tie-line segments only in the non-perspective projections (Figs. 17-4 to 17-6).

c. *Jänecke prism*. If the water content is represented on verticals raised on the Jänecke base diagram of Fig. 17-7, we have a 3-dimensional isothermal diagram similar to Fig. 16-26, but on a square rather than a triangular base. The water content may also be shown approximately on the Jänecke base diagram itself, by a suitable number of contours of constant water content. Finally if a number of Jänecke isotherms of the type of Fig. 17-7 are superimposed, that is, placed one upon another spaced according to temperature, and if their various points are connected into curves of threefold saturation, we have a T/c square prism, in which the height is T and the cross section is the composition square for salt proportions of saturated solutions, the water content being ignored.

d. *Löwenherz diagram*. In Fig. 17-9 the isotherm is plotted in terms of method (f) of Table 17-1, equivalents of salts per fixed quantity, such as 100 moles, of water; this is referred to as the Löwenherz diagram. It resembles closely the orthogonal (base) projection of the pyramid (Fig. 17-4). Although the data are easily plotted in this manner, with the number of equivalents of CD in excess of AB measured from W toward CD and the number of equivalents of AD in excess of CB measured vertically, the quaternary compositions cannot be read back from the plot. As explained in Chapter XVI, the reading of a quaternary composition on a Löwenherz diagram requires a construction based on the knowledge of the total number, N , of salt equivalents per 100 moles of water. Then if the line WQ_1 of Fig. 17-9, for example, is extended away from W to a point Q'_1 , by the method of parallels, so that $Q'_1Q_1/Q_1W = 100/N$, the salt proportions of the quaternary composition Q_1 may be read from the position of Q'_1 in a reciprocal salt square with half-diagonal, $W-(AB)'$, of length $100 + N$. Again, a separate construction is needed for the similar reading of each quaternary point, since the dimensions of the required square will vary, with N , from point to point. The relation between the Löwenherz and the Jänecke diagram is that shown in Fig. 16-23; the Löwenherz and the Jänecke points lie on one line through the point W, but there is no general relation between them in respect to water content, and the significance of their relative position varies from point to point on the superimposed diagrams. The Löwenherz diagram is not a projection of the finite pyramidal figure of Fig. 17-2, and the salts AB, AD, CD, and CB lie at infinity on its

axes. It is rather the orthogonal projection, on a horizontal plane, of a diagram constructed in a square pyramid with its base at infinite distance from the water apex.

2. Isothermal Evaporation

If the unsaturated solution **P** (Fig. 17-2) is evaporated isothermally, the loss of water causes the total composition to change along the straight line **WP** away from **W** into the pyramid. During all subsequent crystallizations, to the final drying-up of the solution, the total composition will always be found on this line, which cuts the base of the pyramid at the point **P'**, the Jänecke projection of **P**, showing the salt proportions. The saturation surface first reached is therefore read from the Jänecke projection (Fig. 17-7), in which it is assumed that the surfaces do not overlap in perspective projection. As the first salt, **CD**, separates on evaporation, the equilibrium saturated solution follows a crystallization path on the **CD** surface, fixed by its intersection with the plane **W-P-CD**. This path is therefore the curve *auwv* of the section of Fig. 17-3. Saturation is first reached at point *u*; when the liquid reaches *w*, the ratio of solid **CD** to liquid = wP_w/P_wCD . When the total water content drops to the line *v-CD*, the liquid reaches the twofold saturation curve *fQ₂* for **L + AD + CD**, at point *v*. For processes involving the quaternary curves it is not necessary, however, to use sections of the space model, since the various projections suffice for the complete representation of the curves.

Except for the question of the relative amounts of phases in equilibrium during the process, the isothermal evaporation of a solution of given salt proportions can best be followed through the Jänecke diagram, the only projection on which the crystallization paths are straight lines, here radiating from the corners in each field (Fig. 17-7). If each of the two invariant points lies within the triangle of its three salts, as in Fig. 17-7, both are solutions congruently saturated with their salts, and both therefore congruent drying-up points of the isotherm. All liquids with salt proportions falling in triangle I dry up at **Q₁** without passing through **Q₂**, to leave a mixture of **AB + CD + CB**, while liquids in triangle II similarly dry up at **Q₂** without passing through **Q₁**, to leave a mixture of **AB + CD + AD**. When the liquid from any field reaches a curve of twofold saturation, it follows the curve toward one of these invariant points, as indicated by the arrows on the figure. These arrows therefore mark the direction of falling vapor pressure, usually also of falling water content. The point *m*, then, on the intersection of the **AB-CD** diagonal with the curve **Q₁Q₂**, must be a "saddle point" in respect to "water content," and the direction followed by liquid on this curve is away from *m* on either side, toward the congruent

drying-up points. The point m similarly falls on the AB-CD diagonal in Fig. 17-4, on the vertical axis in Fig. 17-6(b), and on the AB-CD axis in Fig. 17-9. In the other projections it may be taken usually as the maximum on the Q_1Q_2 curve.

As the solution P in Fig. 17-7, then, is evaporated, it begins to precipitate AB when it reaches the saturation surface for this salt, and the liquid composition moves on the straight line AB- P to meet the curve Q_2mQ_1 at x . The liquid, precipitating both AB and CD, then travels on this curve until it reaches the point Q_1 , when CB begins also to precipitate. When the point Q_1 has just been reached, the solid consists of a mixture of AB and CD in the proportions $(CD-y)/(AB-y)$. At Q_1 the liquid then dries up invariantly to leave a mixture of AB + CD + CB of composition P , and during this invariant process the solid composition lies on the line yP .

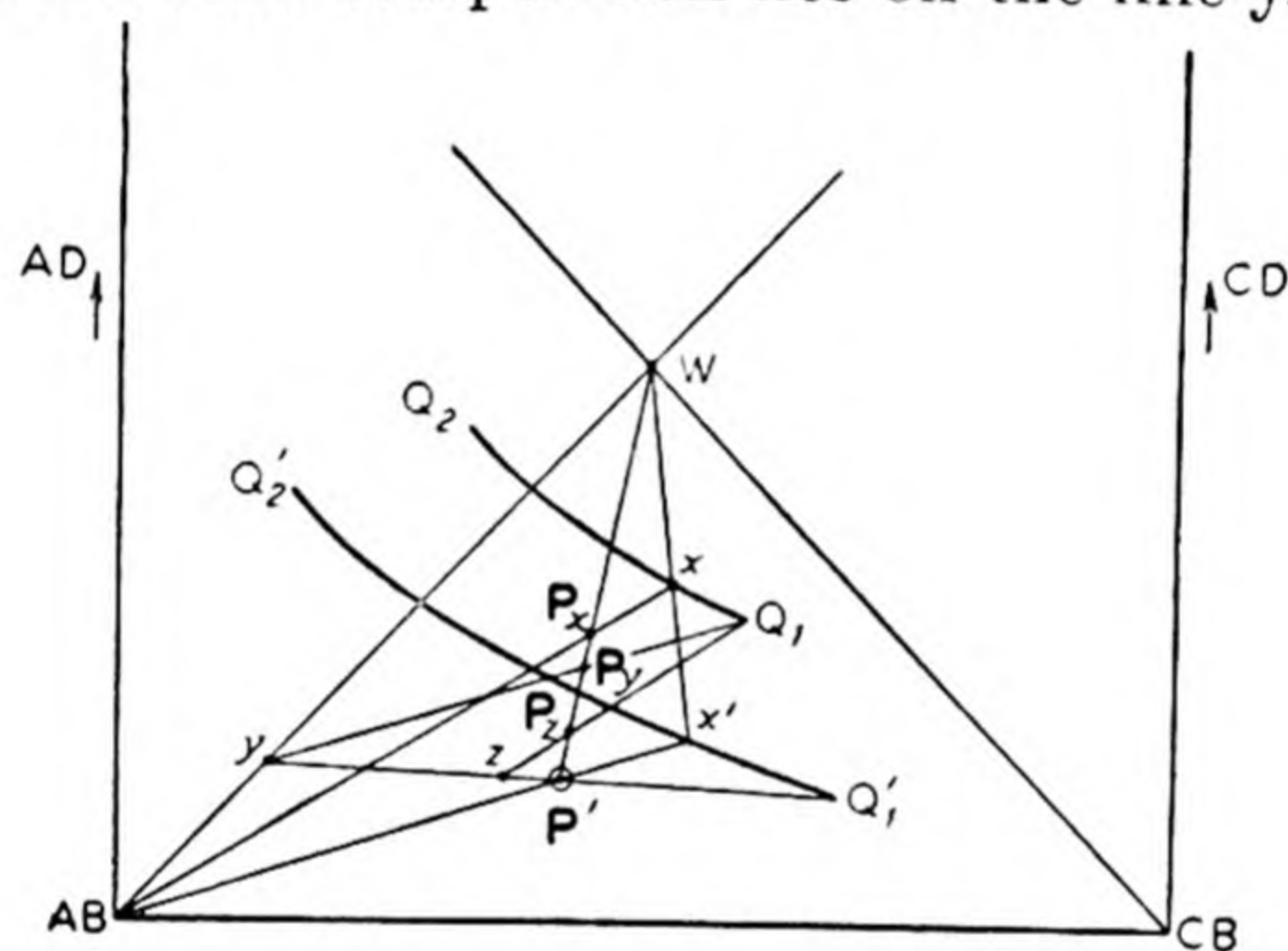


FIG. 17-10. Graphical operation with superposed orthogonal and Jänecke base diagrams.

For the ratio of solid (or solids) to liquid during the evaporation, beginning with the arrival of the liquid at a curve of twofold saturation, such as at the point x , the Jänecke diagram must be used in conjunction with one of the orthogonals. In Fig. 17-10 the curve Q_1Q_2 is shown projected both orthogonally as Q_1Q_2 and perspectively (Jänecke method) as $Q'_1Q'_2$, on the base of the pyramid.¹ The salt proportions of the solution being evaporated are P' . The point x' , where the liquid, precipitating AB, first reaches the curve, is transferred from the Jänecke to the orthogonal curve in the usual way, as point x , on the line $x'W$. Now the intersection of AB- x with $P'W$, or P_x , gives the orthogonal projection of the total composition of the system, with $\%W = 100 P'P_x/P'W$, and the ratio of AB to $L_x = P_xx/(AB-P_x)$. As the liquid travels toward the invariant point, the composition of the mixture of AB + CD is given by the tie-line from the Jänecke curve through P'

¹ For purposes of clarity and convenience the quantitative relations assumed in Figs. 17-(10-13) are not uniform, and not identical with those in Figs. 17-(2-9).

to the diagonal AB-CD, such as point y for the liquid just arrived at Q'_1 . At this point the total composition (orthogonal plot) is P_y , and the ratio of solid to liquid = $P_y Q_1 / y P_y$. For a specified total composition beyond this point, such as P_z , the solid mixture has the composition z , consisting of AB + CD + CB, and the ratio of solid to liquid is $P_z Q_1 / z P_z$. The point x may similarly be fixed on the Löwenherz diagram (Fig. 17-9) by superimposing Löwenherz and Jänecke diagrams and finding the intersection of $x'W$ with the Löwenherz curve $Q_1 Q_2$; but nothing further can be done with the Löwenherz diagram because it lacks tie-lines leading to the pure salts, which lie at infinity.

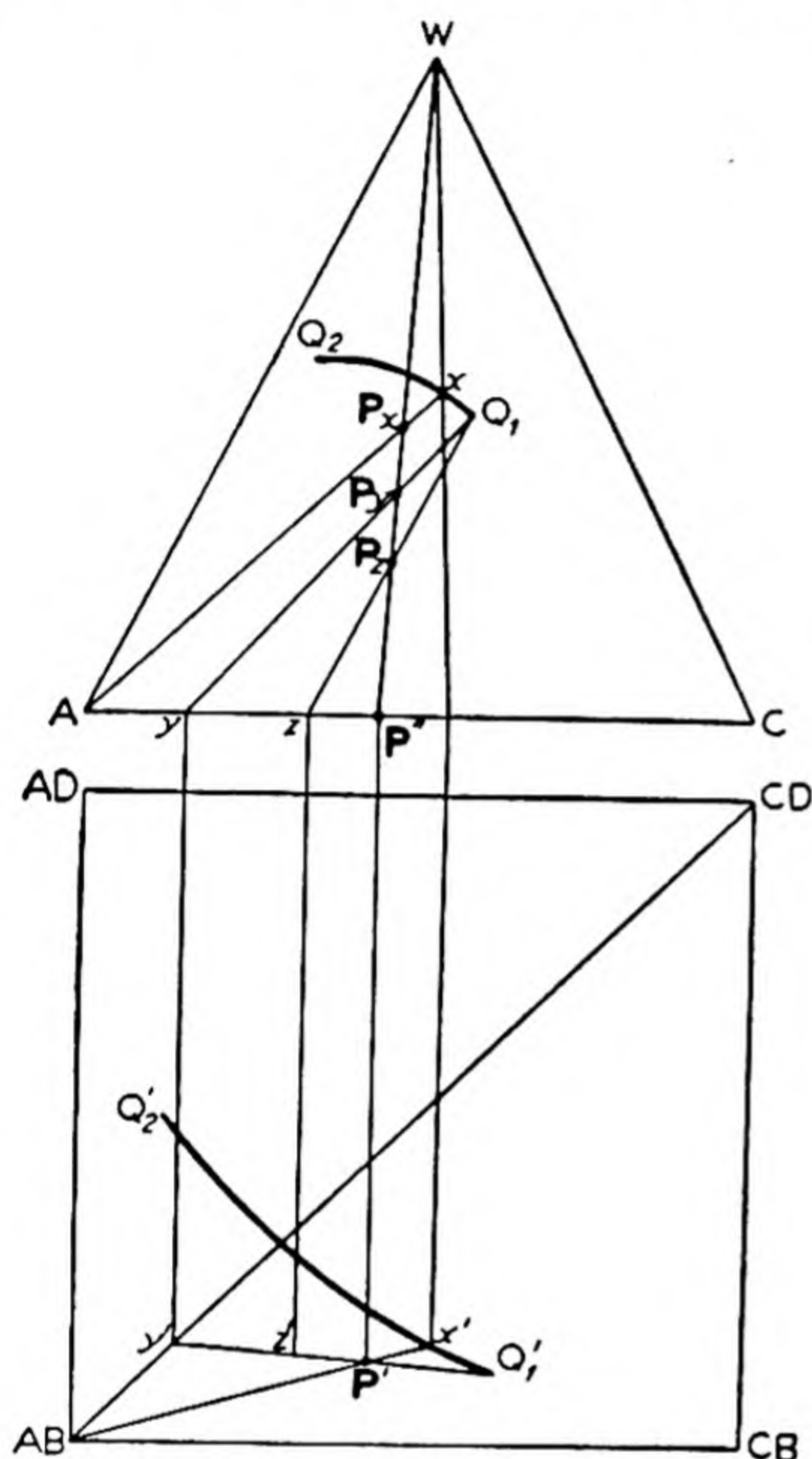


FIG. 17-11. Graphical operation with right plane and Jänecke projections.

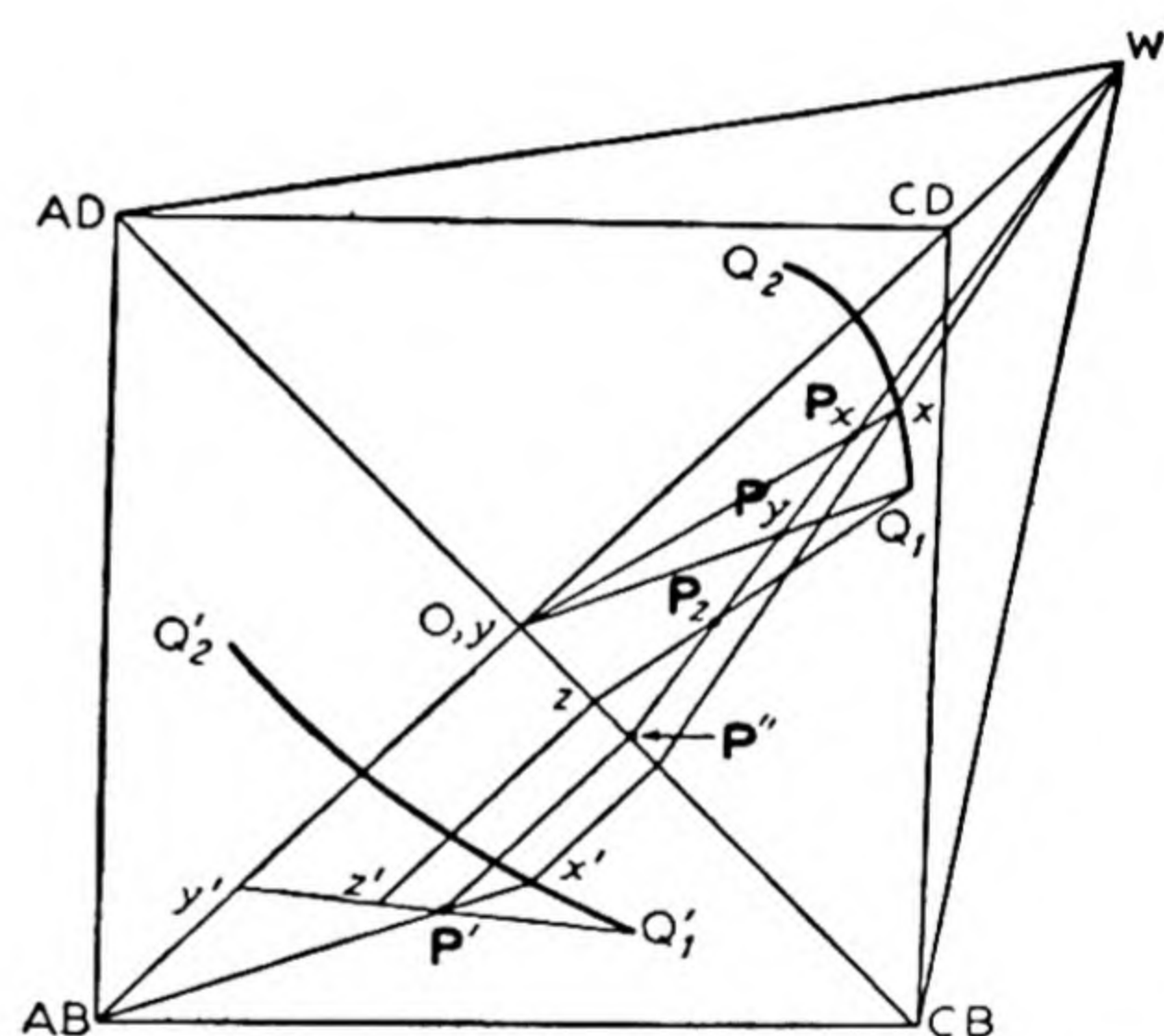


FIG. 17-12. Graphical operation with diagonal plane and Jänecke projections.

The considerations of Fig. 17-10 are repeated in Fig. 17-11, in which the upper diagram is a right plane projection of the curve $Q_1 Q_2$ on the plane of Fig. 17-5(a), while the lower part is the Jänecke base. With P'' fixed on the upper diagram by a vertical from P' , the total composition will always appear, on that projection, on the line WP'' . The point x' is transferred to the right plane curve, point x , as explained under Fig. 17-8, and the intersection of xA with $P''W$ gives the total composition P_x , and hence the total water content and the proportions of the phases. When the liquid reaches Q_1 the Jänecke diagram gives the solid composition as y' ; with this transferred as y , the total composition is fixed as P_y , the intersection of yQ_1 with WP'' . When the water content of the total system drops to P_z , the ratio of solids to liquid = $P_z Q_1 / P_z z$, and the composition of the solid mixture is read

on the Jänecke diagram as z' on the line $y'P'$, by dropping a perpendicular from z .

The Jänecke diagram is used in similar fashion with a diagonal plane projection, that of Fig. 17-6(b), in Fig. 17-12. The total composition on the latter projection falls on the line WP'' . The point x on Q_1Q_2 is transferred from x' as explained under Fig. 17-8. The Jänecke tie-line $AB-P'-x'$ becomes $OP_x x$ on the diagonal plane, since AB appears at O on this plane. When the liquid reaches Q_1 , the solid composition y' also appears (y) as point O in the diagonal plane, since the points AB and CD are superimposed at O ; the total composition is then P_y . Finally, when the water content reaches P_z the ratio of solid to liquid is $P_z Q_1 / P_z z$, and the solid composition is read as z' on the line $y'P'$ of the Jänecke diagram.

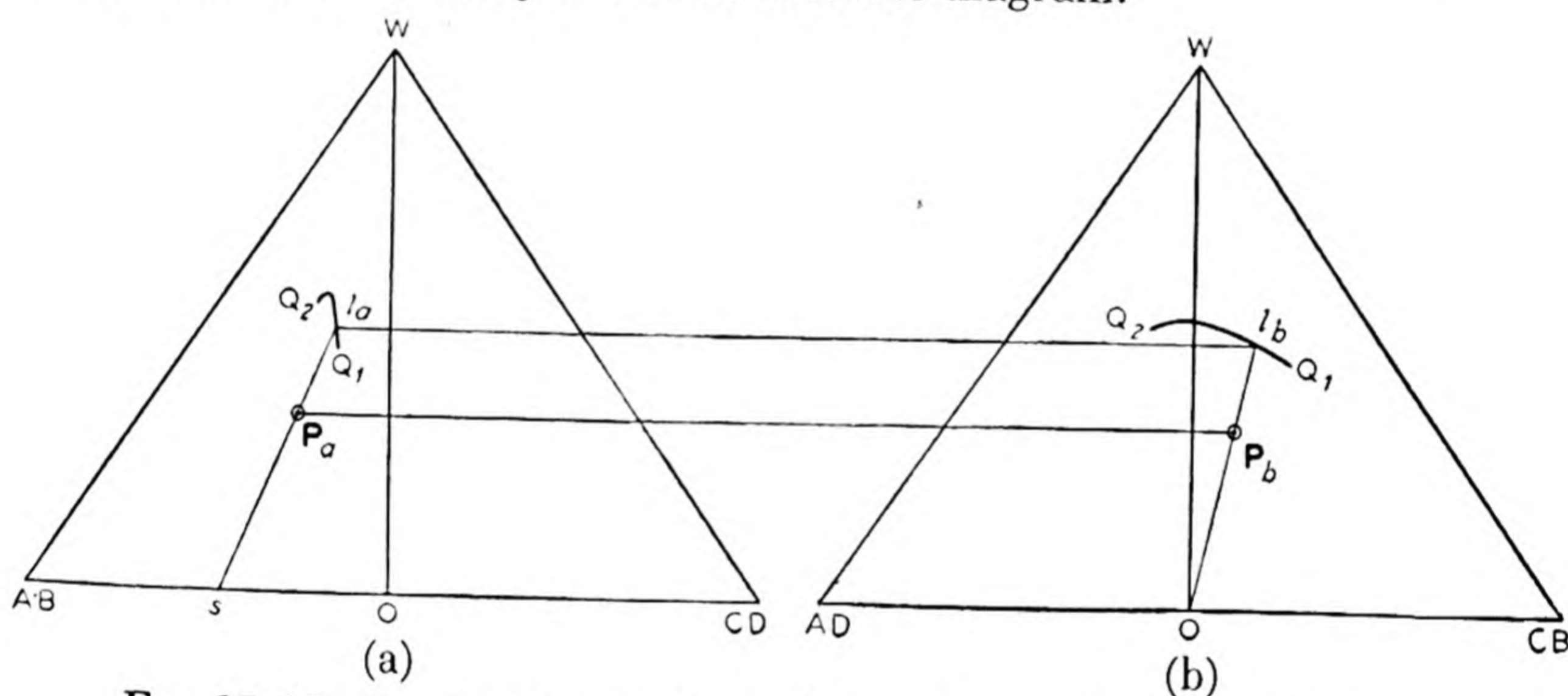


FIG. 17-13. Graphical operation with two diagonal plane projections.

On the constructions of Figs. 17-11 and 17-12 it is seen that for water content between P_x and P_y the solution is in twofold saturation, and for water content below P_y it is in threefold saturation and invariant.

Finally, to find the phase compositions and ratio for the equilibrium $L + \text{two solids}$ from a specified total composition, one of the two projections used must superimpose the two solids. If the solids are AB and CD , for liquid on curve Q_1Q_2 , we may use, for example, a pair of diagonal planes, Fig. 17-13. In this problem P is a point in a space of the nature of Fig. 16-12(b), for liquid saturated with AB and CD . Since the salt mixture, $AB + CD$, is given by point O of Fig. 17-13(b), then the liquid composition is fixed by the line OP_b as l_b on Q_1Q_2 , which then fixes l_a on the (a) plane. Finally the line $l_a P_a$ now fixes the point s on the base of Fig. 17-13(a), giving the proportions of AB and CD . The ratio of solids to liquid is given by the tie-line segments in either plane.²

² Such graphical operations are discussed by F. A. H. Schreinemakers, *Z. phys. Chem.*, 69, 557 (1909), specifically for the use of the orthogonal base projection combined with

Semigraphical solutions of such evaporation problems are possible on the basis of the Jänecke prism already mentioned, in connection with which, it must be noted, however, that the tie-line segments of the vertical sections do not give the phase ratios.^{2a}

3. Congruence of Saturation

In Fig. 17-7, if a solution has the composition (salt proportions) represented by the point O , whether made up from the pair $AB + CD$ or from the pair $AD + CB$, in equivalent proportions, it precipitates CD on isothermal evaporation (just as CD is precipitated on cooling, in Fig. 15-13), and the composition of the residual liquid proceeds to the point m where it dries up invariantly to a mixture of $AB + CD$ in the proportions of point O . The solution m is therefore said to be congruently saturated with respect to the salts AB and CD . All compositions on the diagonal $AB-CD$ dry up at m , behaving like a ternary system consisting of W , AB and CD as components. The section $AB-CD-W$ of the isotherm of Fig. 17-2, or the line $AB-CD$ of Fig. 17-7, is therefore called a **quasi-ternary section**. All other liquids dry up either at Q_1 or at Q_2 . With W_l ("water content") as the analog of T , the Jänecke prism, having W_l as vertical axis on the Jänecke diagram as base, is the analog of Fig. 15-15, and the Jänecke diagram itself, Fig. 17-7, is a "polyhydric projection" of the Jänecke prism, just as Fig. 15-13 is the polythermal projection of Fig. 15-15.

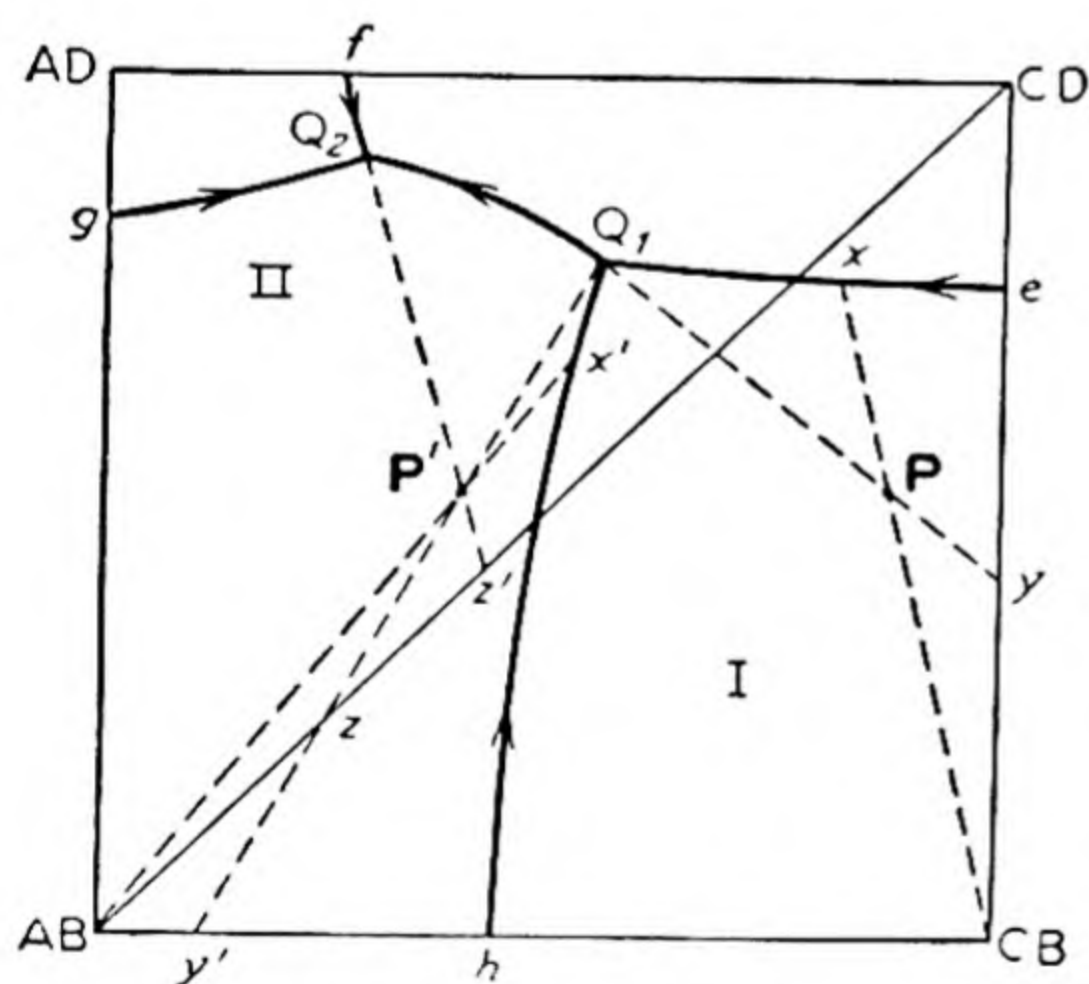


FIG. 17-14. Variation of Fig. 17-7.

At a different temperature, the same system may have the solubility relations shown in Fig. 17-14 (analog of Fig. 15-14). Now Q_2 is congruently saturated, Q_1 incongruently saturated, with its three salts. The arrows show the direction of falling W_l , so that Q_2 is the only W_l -minimum. Since only the pair $AB + CD$ can saturate the same solution simultaneously (curve Q_1Q_2), all solutions must again dry up either to $AB + CD + CB$ or to $AB + CD + AD$; but those in the first triangle dry up incongruently at Q_1 . Q_1 is reached,

a diagonal plane; for other possibilities, see J. E. Ricci and C. M. Loucks, *J. Chem. Educ.*, **15**, 329 (1938). The use of superposed orthogonal and Jänecke base projections has also been proposed by E. V. Sayre, *J. Am. Chem. Soc.*, **71**, 3281 (1949). On the use of juxtaposed projections, see also V. I. Nikolaev, *Compt. rend. acad. sci. U.R.S.S.*, **24**, 556 (1939).

^{2a} The procedure is discussed by Purdon and Slater (Ref. M), Chapters 10, 11. See also E. Jänecke, *Z. anorg. Chem.*, **71**, 1 (1911).

in isothermal evaporation, by all solutions in the quadrangle $AB-Q_1-CD-CB$, either carrying $AB + CB$ along the curve hQ_1 or carrying $CB + CD$ along the curve eQ_1 . Those originating in triangle I lose the liquid phase at the point Q_1 , in the invariant reaction (diagonal reaction, type B), $L + CB \rightarrow AB + CD + W$,[↗] to leave $AB + CD + CB$ so that Q_1 is the incongruent drying-up point for triangle I. When the solution P , for example, reaches x on the curve eQ_1 , a certain quantity of solid CB has precipitated. As the liquid then travels on the curve eQ_1 toward Q_1 , the solid becomes a mixture of CB and CD , with the composition y when the liquid reaches Q_1 . During the invariant reaction at Q_1 , some CB is redissolved with precipitation of AB and CD , so that when the liquid is all consumed the mixed solids have the composition P . If the solids accompanying the solution on reaching Q_1 are removed, as by filtration, the residual liquid proceeds on Q_1Q_2 to Q_2 , precipitating $AB + CD$, to dry up to a mixture of $AB + CD + AD$ at Q_2 , since the total composition, in respect to salts, was changed to Q_1 , a point in the triangle II.

Those solutions reaching Q_1 from the narrow triangle $AB-Q_1-CD$ and hence in II, there lose their solid CB in the invariant reaction and proceed on the curve Q_1Q_2 to Q_2 . Thus P' reaches x' through separation of AB , and then Q_1 with a mixture of AB and CB in the proportion y' . During the invariant reaction CB is redissolved, and the solid changes to a mixture of AB and CD on the point z . As the liquid then travels on the curve Q_1Q_2 the proportion of CD increases so that when Q_2 is reached the solid mixture has the composition z' . Then during the invariant reaction, $L \rightarrow AB + CD + AD + W$,[↗] at the congruent drying-up point Q_2 , the solid mixture moves from z' to a mixture of three solids with the composition P' .

4. Stable Pairs; Conversion of Salts

In both figures (Figs. 17-7 and 17-14) the pair $AB + CD$ is known as the *stable pair*, and the line $AB-CD$ as the stable diagonal. If the solid phases are the anhydrous salts, this expression has exactly the same significance as that of the "stable pair" of the ternary system of the salts alone, as discussed in Chapter XV, under Figs. 15-(21-23). The pair stable as anhydrous salts in contact with aqueous solution is also the pair stable in the non-aqueous system at the same temperature. In the aqueous reciprocal system, however, the solids involved may not all be anhydrous, and the expression "stable pair" then refers to the solubility relations without necessarily implying the same relation in the non-aqueous system. The stable pair, then, in the present connection, is that pair, without regard to hydration, which can saturate simultaneously an aqueous solution.

This stability of salt pairs may be reversed by change of temperature, through the sequence of isothermal relations shown in Fig. 17-15. As T changes, the curve Q_1Q_2 for saturation with the stable salt pair shifts and contracts, vanishing to a point at T_4 , at which the solution is saturated with all four salts. This is a "condensed" invariant point, the transition point in respect to stability of salt pairs. Beyond this temperature, the "reciprocal"

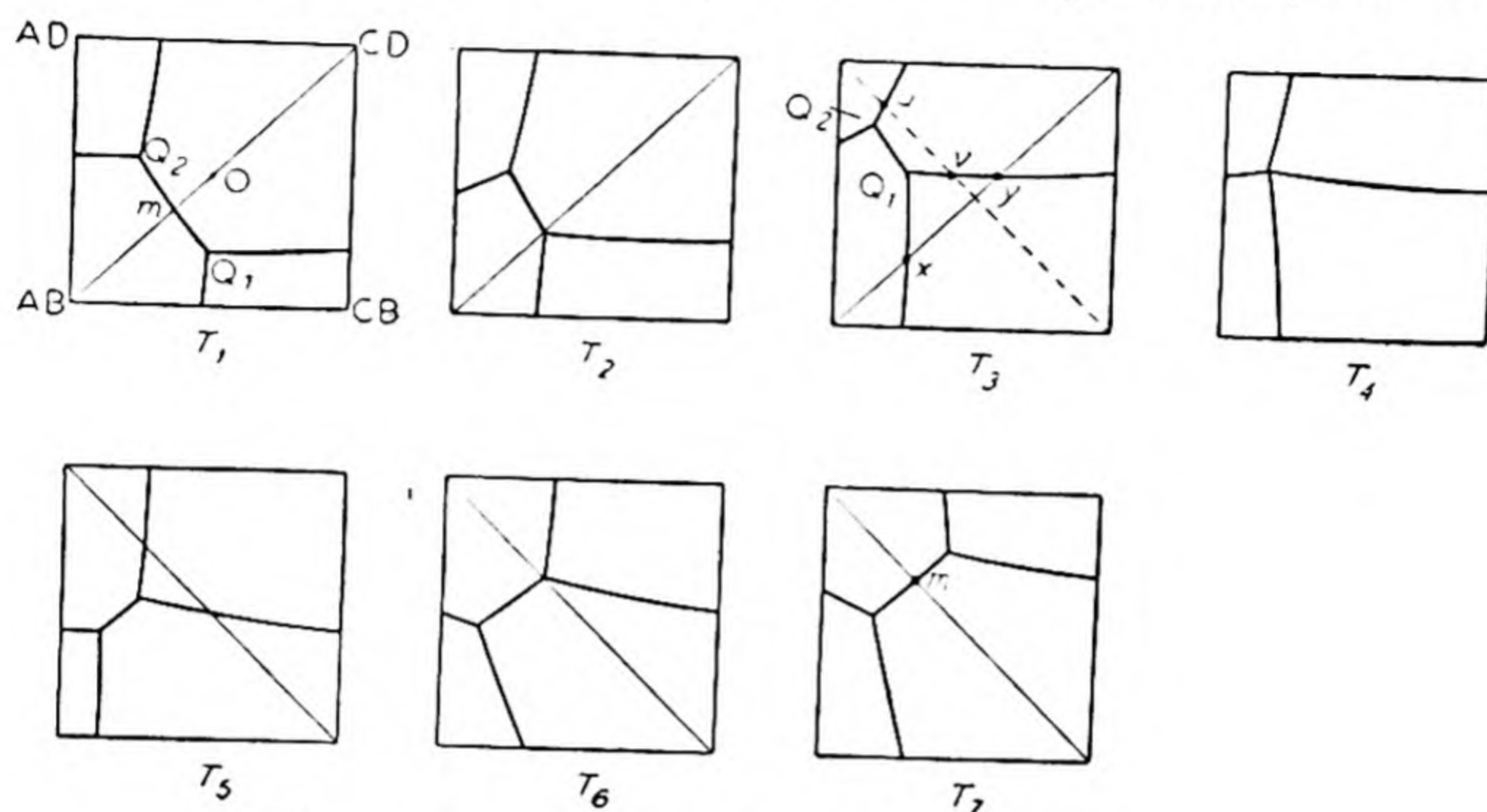


FIG. 17-15. Inversion of pair stability.

curve for saturation with a pair of reciprocal salts, reappears, but in such a way that the opposite salt pair becomes stable. In Fig. 17-15, therefore, the stable diagonal changes from AB-CD below T_4 to AD-CB above T_4 . Van't Hoff³ showed that that pair is the stable pair at any given temperature, which has the smaller product of solubility products (ideally, at any rate). If then we plot the product of K_{AB} and K_{CD} (solubility products) and the corresponding product for the reciprocal pair AD and CB, both as $f(T)$, the intersection of the two curves should give, at least approximately, the transition point for the reversal of pair stability. In the aqueous system $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + 2\text{KCl} \rightleftharpoons 2\text{NaCl} + \text{K}_2\text{SO}_4$, the first pair is stable below, the second above, $\sim 4^\circ$; according to the solubility products the transition was estimated to be at $\sim 10^\circ$ (van't Hoff). In the aqueous system $\text{NaIO}_3 \cdot \text{H}_2\text{O} + \text{KCl} \rightleftharpoons \text{NaCl} + \text{KIO}_3$, the first pair is stable below $37-39.5^\circ$ (observed); calculated, $38-39^\circ$.⁴ This solubility criterion of stability of pairs is essentially comparable to that in non-aqueous reciprocal salt systems, involving lattice parameters and heats of formation (Chapter XV Section F).

Moreover, a solution saturated with the stable pair AB + CD may be made from the two salts and water, at temperatures below T_2 , but not

³ J. H. van't Hoff and L. T. Reichert, *Z. phys. Chem.*, **3**, 482 (1889).

⁴ T. G. Sahlstein, *Bull. comm. geol. Finlande*, **104**, 104 (1934).

between T_2 and the transition point T_4 . At T_3 , for example, if the two salts AB and CD, in any proportion whatever, are added to water until they are both present in excess, the solution has the composition Q_1 and is saturated not only with the pair but also with CB. The interval T_2 – T_4 , between the transition point T_4 and the temperature when the stable diagonal cuts the curve Q_1Q_2 , is known as the transition interval of the salt pair; the interval for the opposite pair is therefore T_4 – T_6 . Below T_2 the solution m , as stated above, is congruently saturated with the stable pair AB + CD and may be obtained directly from the two salts + water; the isotherm, in other words, has a quasi-ternary diagonal only outside the transition interval.

Neither of the salts AD and CB can be made, isothermally, from the stable pair AB + CD, below T_2 . In the transition interval T_2 – T_4 , unsaturated solutions made from the stable pair, and with compositions between x and y , will produce CB on evaporation, but the yield of pure CB is limited by the relative positions of the curves; it cannot in general be large because of the smaller product of the solubility products of the stable pair. On the other hand, the stable pair can be made from AD + CB at any temperature below T_4 . If, at T_3 , a solution is made from the unstable pair with composition between u and v , pure CD is the first product on isothermal evaporation. If, moreover, the total composition falls in the triangle CD– Q_1 – Q_2 , the second product is AB, and AD appears, as a third product, only when the evaporation is carried to point Q_2 . At T_1 , below T_2 , a 1:1 mixture of AD and CB, giving composition O at the center of the square, is completely transformed to the pair AB + CD upon being stirred with any quantity of water, followed by isothermal evaporation, the last liquid to dry up being m .

As just implied, a salt of the stable pair may be produced from the unstable pair isothermally even without evaporation. If, for example, the salts AD and CB are taken in the proportion P in Fig. 17-16, and treated with water, the solution is unsaturated if the water content is greater than that which would be read from the isohydre ww' , on the CD saturation surface, through P. If the water content is smaller, the solution would be supersaturated with respect to CD. Then CD will separate and the salt proportions of the solution will change along the line CD–P away from CD, until it becomes saturated at some point l . The composition of the liquid l , both for salt proportions and for water content, and the relative amount

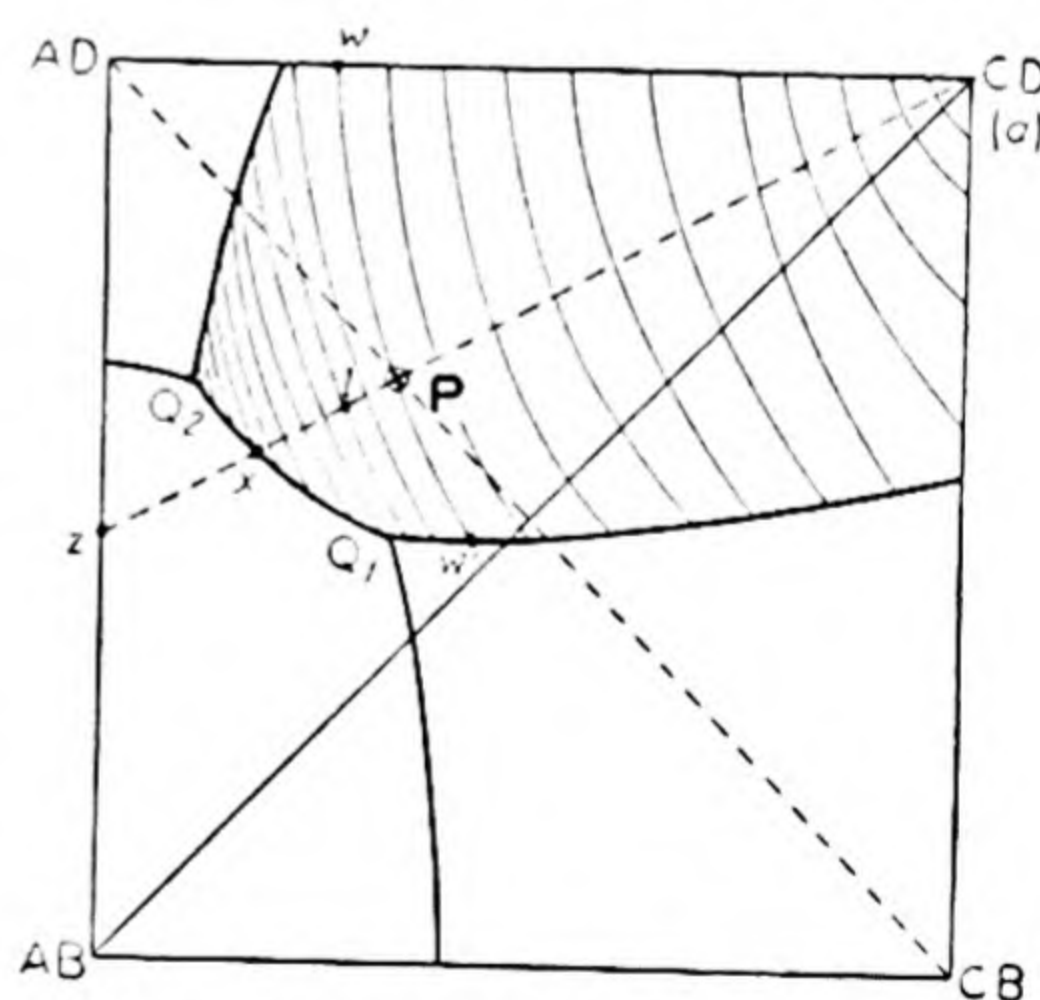


FIG. 17-16. Effect of water content.

of solid CD formed, could be obtained through a section of the pyramid (similar to Fig. 17-3) passing through W, P and CD (Fig. 17-17). If the water content is still lower, such as P_2 , falling between the lines x -CD and y -CD of this section, the equilibrium state will be one of three phases, a liquid on Q_1Q_2 and a mixture of AB and CD, while if the water content is P_3 , below the line y -CD, there will be four phases, the invariant liquid Q_2 and three solids, AB, CD, and AD, at equilibrium. The limiting values of water content for these conditions may be obtained graphically as already explained under Figs. 17-(10-12), especially 17-11 and 17-12, and under Fig. 17-13 for the region of P_2 .

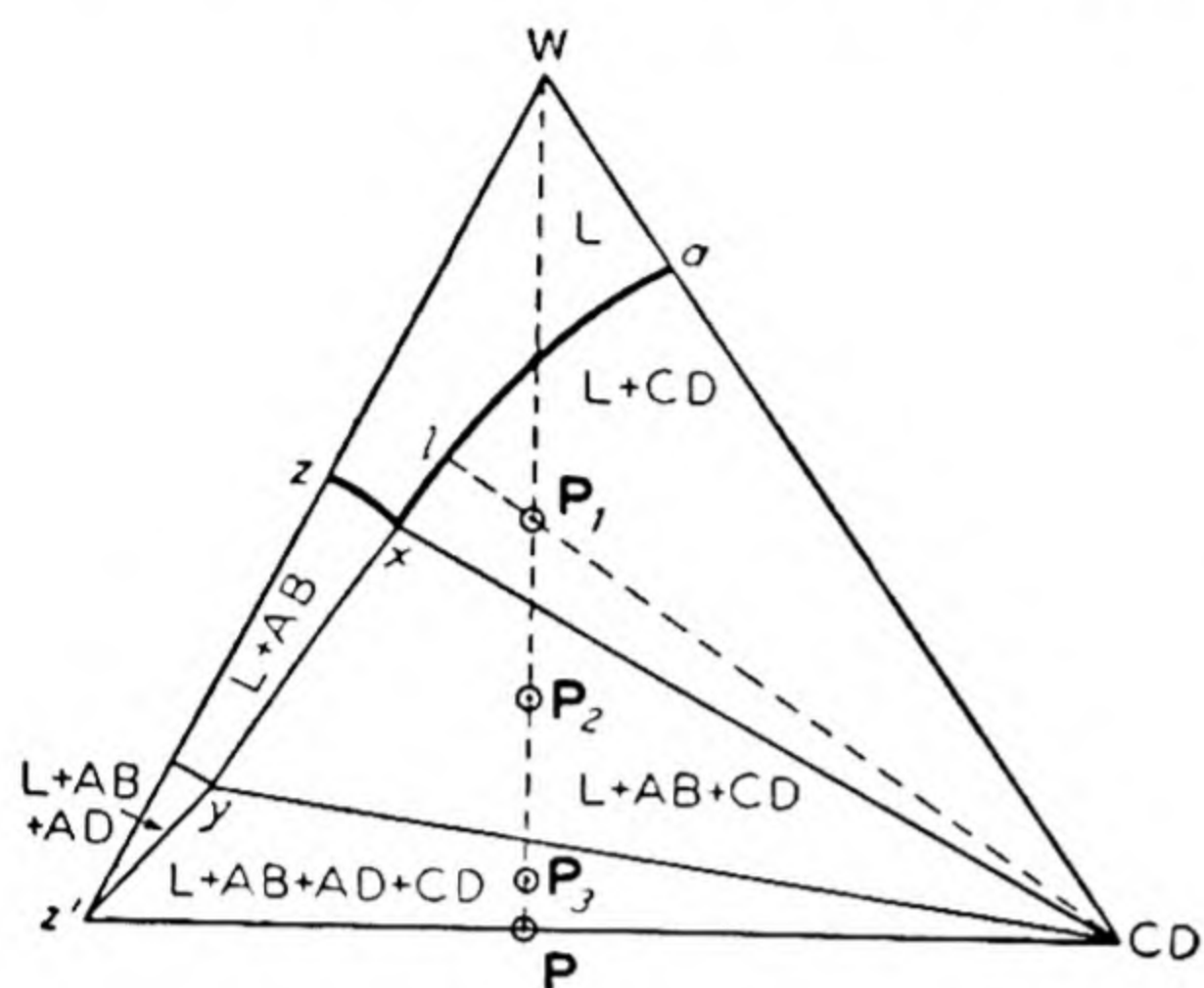


FIG. 17-17. Section of Fig. 17-16.

A comparison of Figs. 17-7, 17-14, and 17-15 with Figs. 15-13, 15-14, and 15-23, respectively, again brings out the analogy between W_1 as the isothermal variable for the condensed aqueous salt systems and T as the isobaric variable in the non-aqueous ternary system. We see also the analogy between the variable T for the isobaric (or condensed) quaternary system and P for the non-aqueous ternary system, in the changes represented by Figs. 17-15 and 15-23.

C. Examples

The aqueous system $\text{NaCl} + \text{NH}_4\text{HCO}_3 \rightleftharpoons \text{NaHCO}_3 + \text{NH}_4\text{Cl}$ at 15° is shown (schematically) in a Löwenherz diagram (Fig. 17-18(a)) and in a Jänecke projection (Fig. 17-18(b) ⁵). The stable pair is $\text{NaHCO}_3 + \text{NH}_4\text{Cl}$. If mixtures of NaCl and NH_4HCO_3 , in proportions between u and v , are treated with a quantity of water insufficient for complete solution, solid NaHCO_3 may be obtained as sole solid phase. If the original salts are taken in the proportion P, on the line NaHCO_3 - Q_1 , the solution can be concentrated to the point Q_1 before the solid NaHCO_3 becomes contaminated with any other salt.

Fig. 17-19 (Jänecke diagram) shows, schematically, the aqueous system $\text{K}_2\text{SO}_4 + \text{BaCO}_3 \rightleftharpoons \text{K}_2\text{CO}_3 + \text{BaSO}_4$, at room temperature.⁶ The stable pair is $\text{K}_2\text{SO}_4 + \text{BaCO}_3$ up to the melting points. In the isotherm shown,

⁵ P. P. Fedotieff, *Z. phys. Chem.*, **49**, 162 (1901); E. Toporescu, *Compt. rend.*, **174**, 870 (1922).

⁶ W. Meyerhoffer, *Z. phys. Chem.*, **38**, 307 (1903); **53**, 513 (1905).

the pair is in its transition interval (T_5 of Fig. 17-15). If water is added to the mixture $K_2SO_4 + BaCO_3$, both salts being in excess, the point Q_1 is obtained, a solution saturated with $BaSO_4$ in addition to K_2SO_4 and $BaCO_3$.

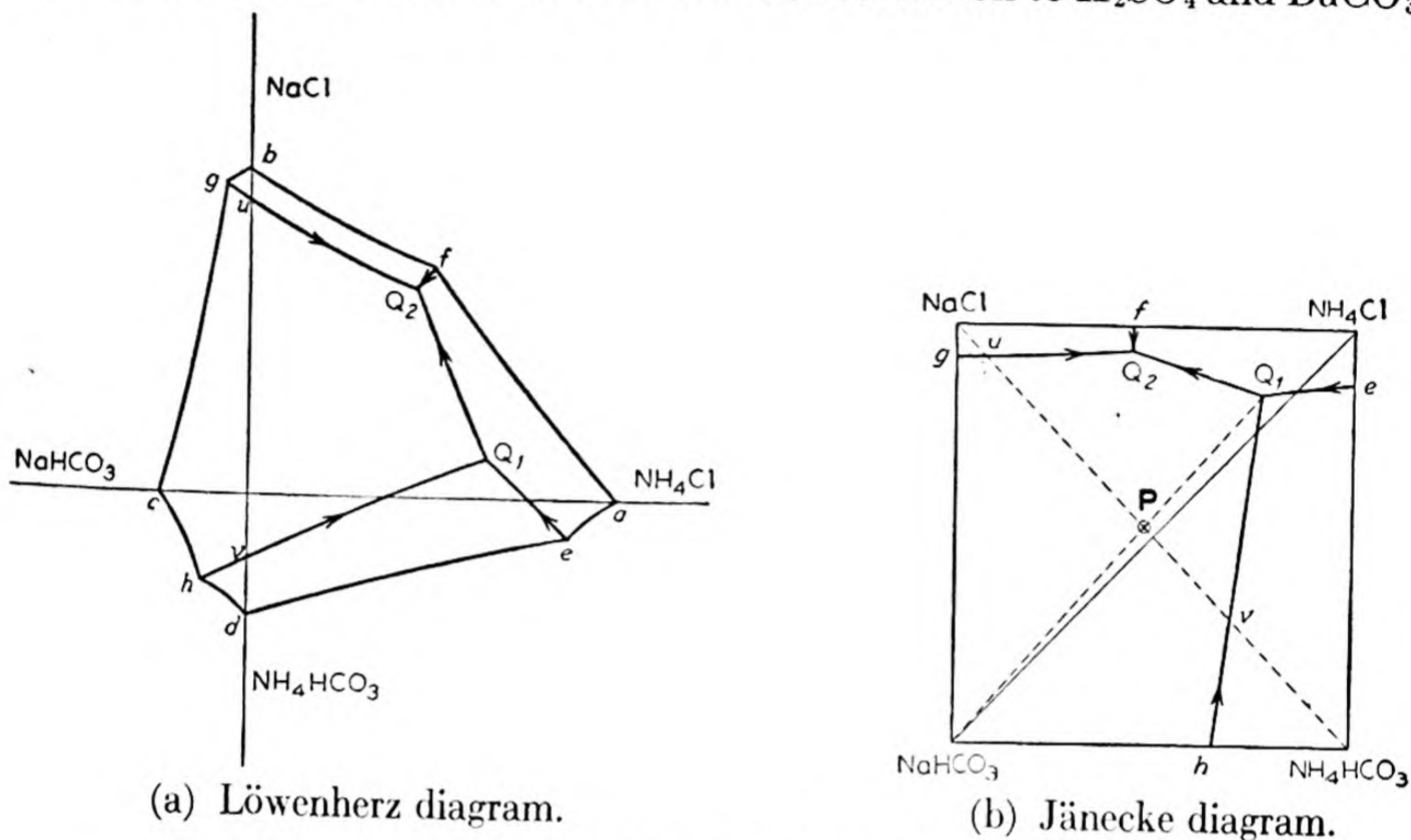


FIG. 17-18. System $NaHCO_3$ - NH_4Cl - H_2O , at 15° .

The actual solubilities of the barium salts are so low that points f , Q_1 , Q_2 , and h are practically indistinguishable from the K_2SO_4 - K_2CO_3 side of the diagram; this region is therefore exaggerated to show the relations. The curve Q_1e is known as the curve of Guldberg and Waage, who studied it in connection with the establishment of the law of mass action.⁷ This solution is saturated with both $BaCO_3$ and $BaSO_4$, and therefore the ratio of carbonate to sulfate, or " K_2CO_3/K_2SO_4 ," in the solution, should be constant at constant T , if the solubility products are constants. At 100° , the ratio ranges from 1.8 to 3.7 as the total concentration of the salts varies from 35.7 to 4.0 moles per 1000 moles of water.

If two (Jänecke) isotherms, such as Figs. 17-7 and 17-14, are superimposed, we have the basis for a cyclic crystallization process for the conversion of unstable salt pair to stable salt pair, such as in the production

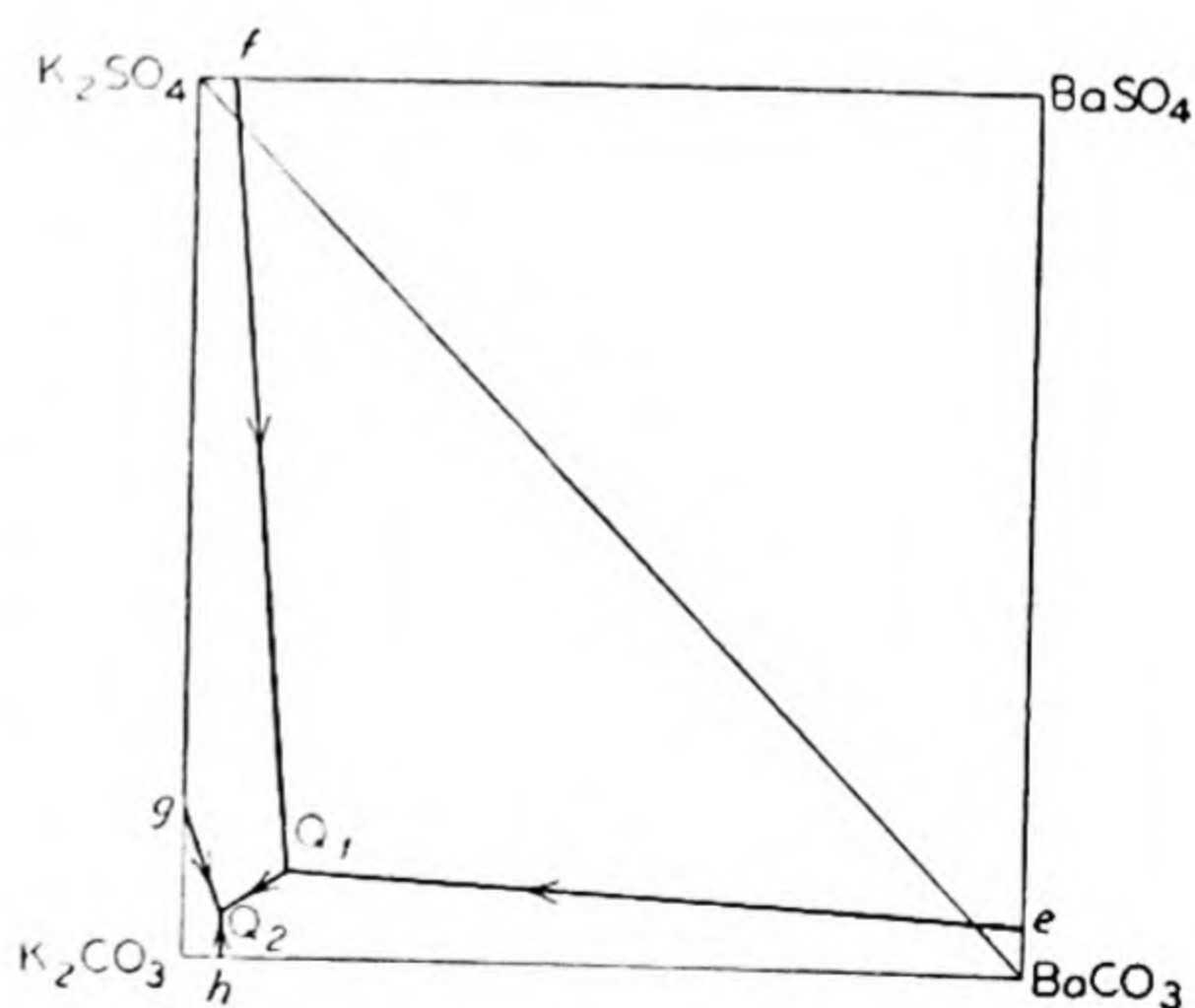


FIG. 17-19. System K_2SO_4 - $BaCO_3$ - H_2O , at room temperature.

⁷ C. M. Guldberg and P. Waage, *J. prakt. Chem.*, **128**, [20], 91 (1879).

of KNO_3 by conversion from $\text{KCl} + \text{NaNO}_3$ ⁸ (Fig. 17-20 at 5° and 100°). $\text{NaCl} + \text{KNO}_3$ is the stable pair at both temperatures; Q_2 and Q'_2 are congruently saturated, at both temperatures; Q'_1 , at 5° , is just congruently saturated, while Q_1 , at 100° , is not.

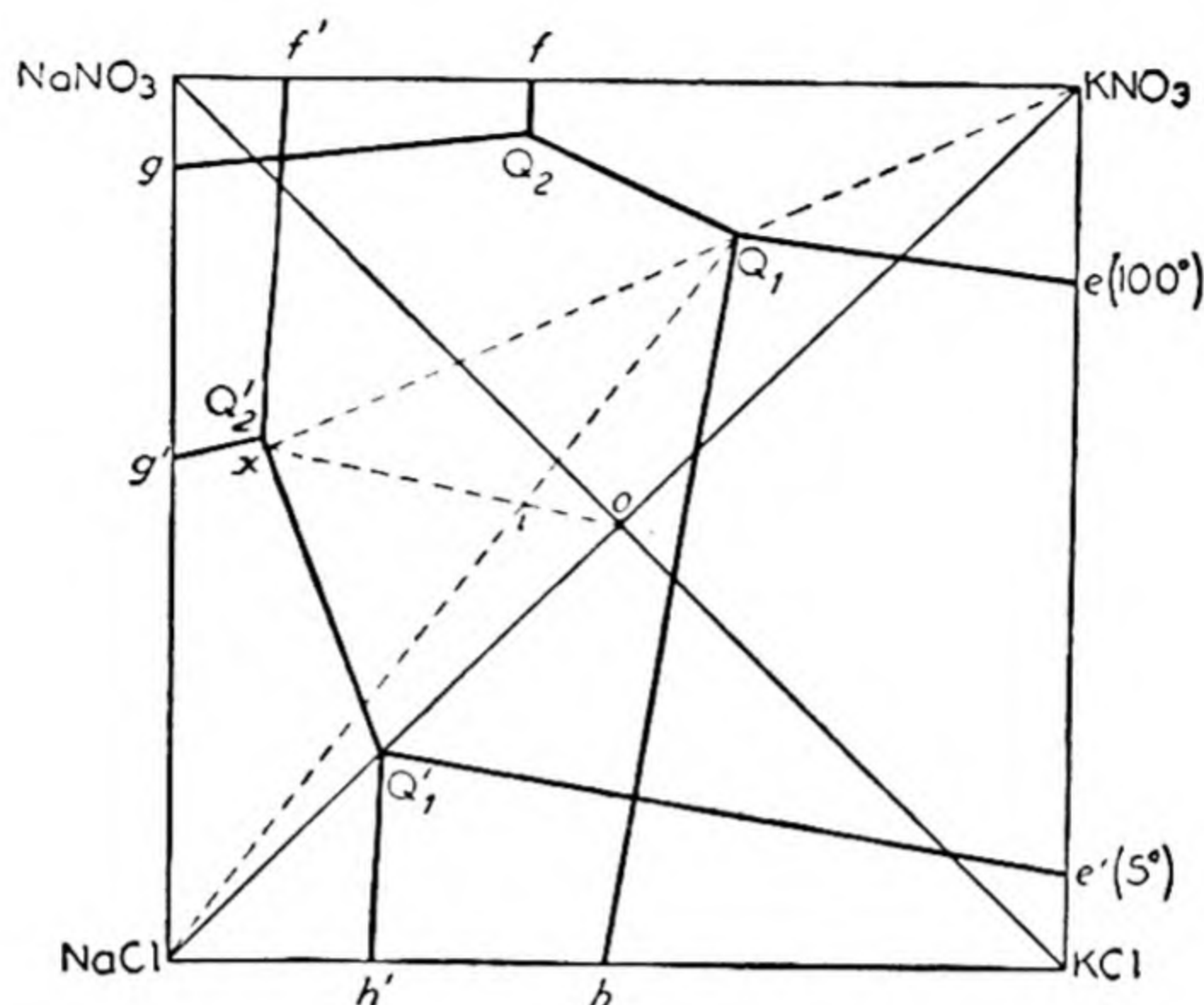


FIG. 17-20. System $\text{NaCl-KNO}_3\text{-H}_2\text{O}$.

If a solution made from NaNO_3 and KCl in equivalent proportions (o) is evaporated at 100° , it precipitates NaCl first and reaches Q_1 along the curve hQ_1 carrying NaCl and KCl . If the solids are now removed by filtration, and the solution, Q_1 , cooled to 5° , this solution lies deep within the KNO_3 field at this temperature. Moreover, the number of moles of water per mole of salt for saturation at 5° , along the curve $Q'_1Q'_2$, the edge of the KNO_3 field, is much greater than the corresponding value at Q_1 at 100° . Hence this solution, cooled to 5° , will precipitate a large proportion of KNO_3 , but it will come to equilibrium only when a certain amount of NaCl is mixed with the KNO_3 because the water content at Q_1 (100°) brings the total composition to a point corresponding to P_2 in Fig. 17-17, at 5° , with respect to point x , the intersection of the line $\text{KNO}_3\text{-}Q_1$ and the curve $Q'_1Q'_2$. Hence, before the Q_1 filtrate is cooled, enough water is added to it (0.37 mole of water per mole of salt in Q_1) to bring its water content up to the line $x\text{-CD}$ of the section of Fig. 17-17. This produces a maximum precipitation of KNO_3 without contamination with NaCl , actually 0.56 mole of KNO_3 per mole of salt in Q_1 . The KNO_3 produced at 5° is then filtered off and the solution x , called the nucleus solution, is now used as the basis of the following cycle of operations.

The compositions of the important solutions involved are given in Table

⁸ W. Reinders, *Z. anorg. Chem.*, **93**, 202 (1915).

17-2. The composition of the nucleus solution differs from point Q_1 by a deficiency of 0.56 mole of KNO_3 and an excess of 0.37 mole of water.

TABLE 17-2. COMPOSITIONS IN MOLES FOR FIG. 17-20

		K^+	Na^+	NO_3^-	Cl^-	H_2O
At 100°	Q_1 ($KNO_3 + NaCl + KCl$)	0.62	0.38	0.80	0.20	1.81
	Q_2 ($KNO_3 + NaCl + NaNO_3$)43	.57	.975	.025	1.24
At 5°	Q'_1 ($KNO_3 + NaCl + KCl$)23	.77	.22	.78	6.50
	Q'_2 ($KNO_3 + NaCl + NaNO_3$)12	.88	.57	.43	4.80
Solution x	($KNO_3 + NaCl$)	0.06	0.38	0.24	0.20	2.18

To the quantity of solution x (nucleus) here tabulated is added 0.56 mole of each of the solid reactants (KCl and $NaNO_3$, to be converted into the products $NaCl$ and KNO_3), resulting in a composition i , on the line xo . This composition is equivalent to solution Q_1 with an excess of 0.56 mole of $NaCl$ and 0.37 mole of H_2O , per mole of salt in Q_1 . Point i is therefore fixed as the intersection of the line xo with the line $NaCl-Q_1$. Evaporation of 0.37 mole of H_2O from this solution at 100° therefore causes precipitation of 0.56 mole of $NaCl$, leaving solution Q_1 . The $NaCl$ is removed, the filtrate Q_1 is diluted with 0.37 mole of H_2O per mole of salt present, and it is cooled to 5°, producing 0.56 mole of KNO_3 and the quantity of solution x tabulated above.

This cycle may be repeated, with addition of more mixture o each time, until the mother liquor (nucleus solution) becomes too impure. The efficiency of the method is seen to depend on the fact that while Q_1 lies deep within the KNO_3 field at 5°, so that the precipitation of KNO_3 on cooling is abundant, the original mixture, added to the nucleus solution, gives a solution i deep within the field of the other product, $NaCl$, at 100°, with little evaporation needed, at that temperature, to bring it to Q_1 .

D. Compounds

1. We shall illustrate relations involving double salts and hydrates with two isotherms (25° and 55°) of the system $MgCl_2-K_2SO_4-H_2O$.

a. Fig. 17-21 (Jänecke diagram) shows the isotherm at 25°.⁹ There are seven solid phases, each with its own field, labeled A for K_2SO_4 , B' for $MgSO_4 \cdot 7H_2O$, B for $MgSO_4 \cdot 6H_2O$, C for $MgCl_2 \cdot 6H_2O$, D for KCl , D_1 for carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, and D_2 for schoenite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. Both double salts are incongruently soluble, so that the points for their compositions, D_1 and D_2 , do not fall within their fields; but all crystallization paths for isothermal removal of water radiate from the salt composi-

⁹ E. Jänecke, *Z. anorg. Chem.*, **100**, 161, 176 (1917); **102**, 41, **103**, 1 (1918); reviewing the work of van't Hoff, Meyerhoffer, and others.

tions of the respective separating solid phases. There are five isothermally invariant points. All but point 4 are incongruently saturated; there are no saddle points, or solutions congruently saturated with two solids. Point 4, congruently saturated with C, B and D_1 , is the W_t -minimum of the isotherm, and the congruent drying-up point for all solutions with original

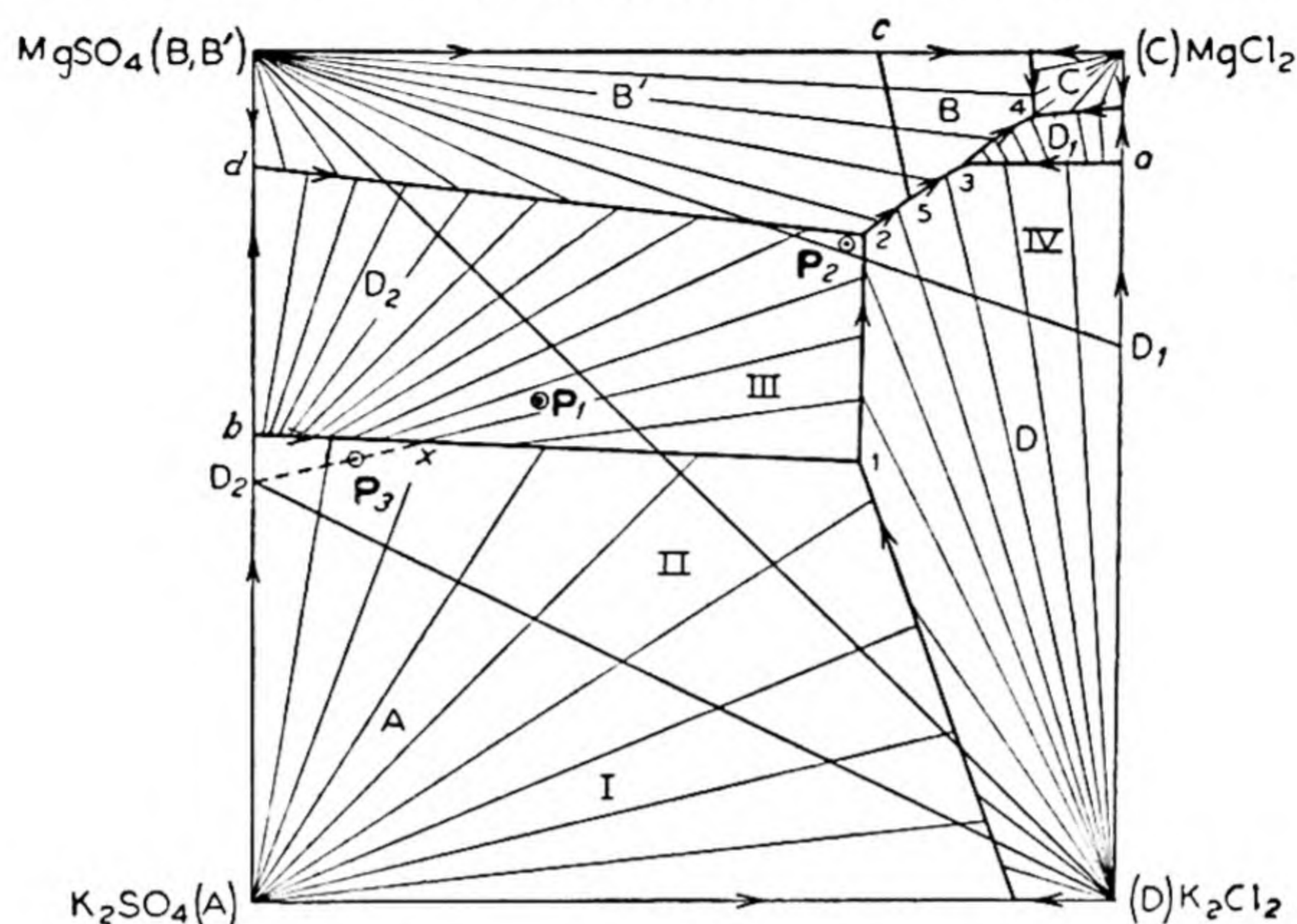


FIG. 17-21. System $\text{MgCl}_2\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$, at 25° .

compositions in triangle IV. The points 1, 2, and 3 are the incongruent drying-up points for solutions in triangles I, II, and III, respectively. Point 5 is the invariant point for the reaction $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O}$, in contact with solution saturated with KCl, and is not even an incongruent drying-up point. The curve $c5$ is an isopiestic dehydration curve of the type discussed in Chapter XVI-E; the twofold saturated solution on this curve is, under conditions of complete equilibrium, isothermally "inevaporable." Two other "odd" crystallization curves are $a3$ ($D-$, D_1+) and $b1$ ($A-$, D_2+); all the rest are even, with positive crystallization of both salts.

Solutions in a triangle of any particular number must reach and dry up at the invariant point of corresponding number. But they may or may not pass other invariant points in their course to their final drying-up points. Each invariant is reached by solutions in the area defined by its four phases. These areas are triangles for points 4 and 5, namely, $\text{MgSO}_4\text{--MgCl}_2\text{--}D_1$ and $\text{MgSO}_4\text{--}5\text{--KCl}$, respectively, and quadrangles for the others, which are invariant points of the diagonal type: AD_21D for point 1, $B'2DD_2$ for point 2, and $B3D_1D$ for point 3. Hence the solution P_1 , in triangle II and in the D_2 field, reaches only point 2 (*via* curve 12) where it dries up; but solution P_2 , in the D_2 field but in triangle IV, passes points 2, 5, 3 before reaching

its drying-up point at 4. It reaches point 2 along curve $d2$, carrying D_2 and B' ; on losing D_2 at point 2, it travels from point 2 to point 5, carrying B' and D ; at point 5, B' is dehydrated to B , and then the solution moves on to point 3. Here it loses its KCl solid phase (D) and travels on curve 34 carrying $B + D_1$, drying up at point 4 to $B + C + D_1$.

The curve $b1$ is reached by all solutions in triangle $Ab1$, but those in the region D_2b1 , such as P_3 , do not reach point 1, since they lose the K_2SO_4 solid when the tie-line through liquid and total composition (P_3) passes through D_2 (point x for P_3); the solution then travels across the D_2 field, precipitating more D_2 , to one of the other two boundaries of this field, finally reaching point 2, which is the drying-up point if the salt proportions are in II. In the same way liquids reaching curve $a3$ from the region D_1a3 , with precipitation of KCl , lose KCl at the expense of carnallite (D_1) as they travel on the curve toward point 3; but when the solid becomes pure D_1 , the liquid leaves the curve and crosses the D_1 field, finally reaching point 4. The reactions at the incongruent drying-up points are: at point 1, $L + A \rightarrow D_2 + D + H_2O$; at point 2, $L + D_2 \rightarrow B' + D + H_2O$; at point 3, $L + D \rightarrow B + D_1 + H_2O$.

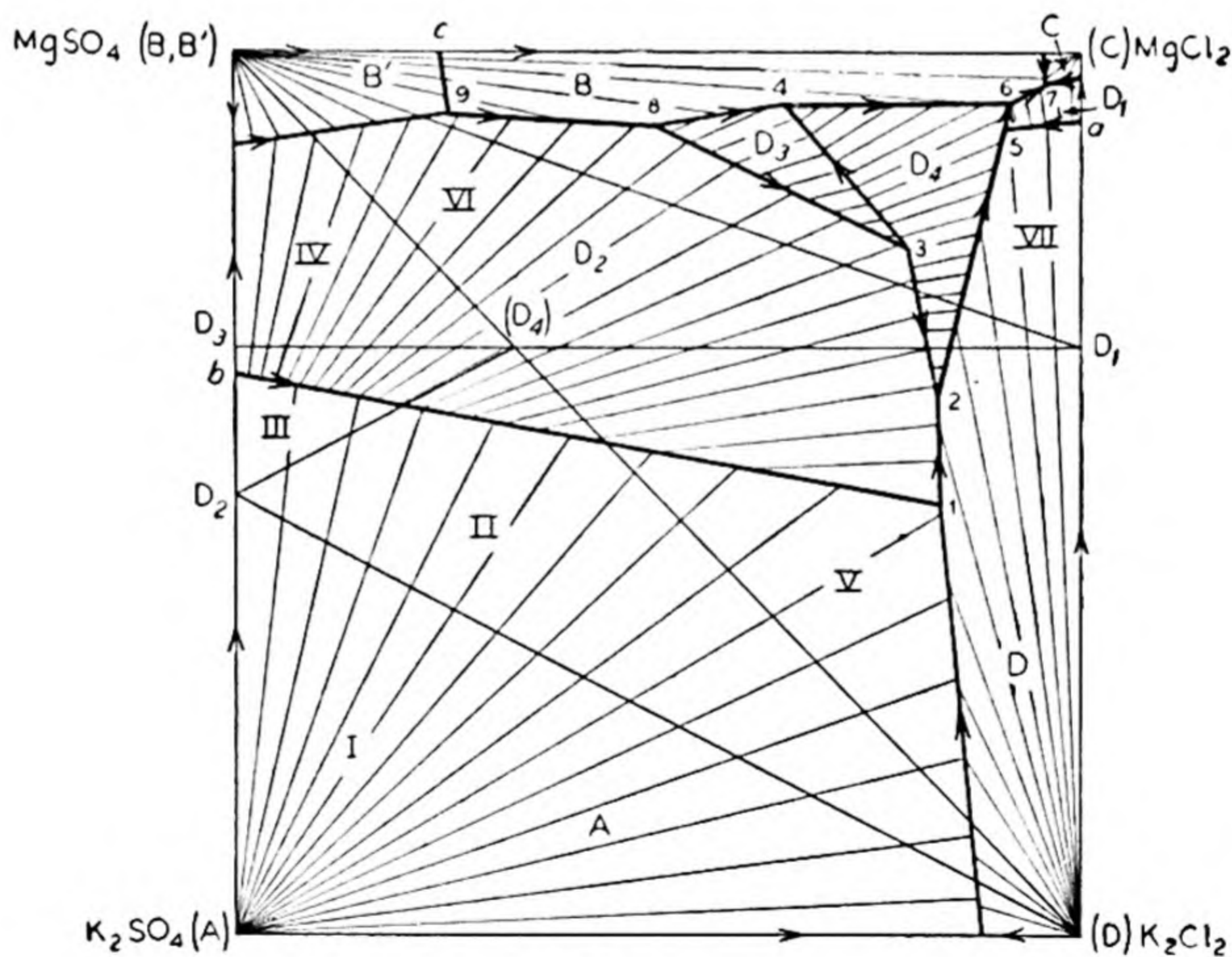


FIG. 17-22. System $MgCl_2$ - K_2SO_4 - H_2O , at 55° .

b. Fig. 17-22 shows the 55° isotherm.¹⁰ There are now four double salts, all incongruently soluble. The tetragene salt kainite, D_4 , or $KCl \cdot MgSO_4 \cdot 3H_2O$, is not present in the system at 25° , although in the quinary system

¹⁰ Diagram as used by Blasdale in Ref. C, p. 147.

formed by addition of NaCl as a fifth component, it does appear as a saturating salt phase even at 25°.

The isotherm shows nine solids and nine fields: A, K_2SO_4 ; B', $MgSO_4 \cdot 6H_2O$; B, $MgSO_4 \cdot H_2O$; C, $MgCl_2 \cdot 6H_2O$; D, KCl; D₁, carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$; D₂, leonite, $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$; D₃, langbeinite, $K_2SO_4 \cdot 2MgSO_4$; D₄, kainite, $KCl \cdot MgSO_4 \cdot 3H_2O$. Kainite is incongruently soluble, and hence the point D₄ lies outside the D₄ field for saturation with this solid phase. Again, of the nine invariant points, only one, point 7, is congruently saturated, for $MgSO_4 \cdot H_2O + MgCl_2 \cdot 6H_2O + \text{carnallite}$; it is therefore the only W_l -minimum of the isotherm. There are seven triangles of three solids representing possible mixtures upon complete evaporation at this temperature; $MgSO_4 \cdot 6H_2O$ is not part of any triangle, so that for the triangles the $MgSO_4$ corner means the monohydrate B. A solution in any particular triangle reaches and dries up at the invariant point of corresponding number, incongruently in every case except point 7 for triangle VII. Points 8 and 9 are never drying-up points, since their solids do not form triangles in the diagram. The directions on the curves (arrows) are uniquely determined by the positions of the solids and invariant liquids, since all crystallization paths are straight lines. Each invariant point is reached by solutions with compositions originally in the area of its four phases. This means that there will be more than one way in which a particular drying-up point may be reached.

The curves of odd crystallization, besides the dehydration curve $c-9$, are: curve $a-5$ (D[−], D₁⁺), curve $b-1$ (A[−], D₂⁺), curve $3-2$ (D₂[−], D₄⁺), curve $8-3$ (D₂[−], D₃⁺), and curve $3-4$ (D₃[−], D₄⁺).

In illustration we shall consider solutions reaching point 8, which is not a drying-up point, so that the liquid phase is never consumed in the invariant reaction at this point. The phase reactions during isothermal evaporation at points 9 and 8 are in fact of a type already discussed, in which the liquid is not only invariant in composition but also invariable, or constant in actual amount, inasmuch as the solids undergoing reaction at these points do not involve all the salt components (equilibria of lower order). At point 9 the phase reaction is merely $MgSO_4 \cdot 6H_2O(B') \rightarrow MgSO_4 \cdot H_2O(B) + W$,[↗] in presence of a liquid containing chloride and also saturated with leonite, $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O(D_2)$. At point 8 the reaction is $MgSO_4 \cdot H_2O(B) + K_2SO_4 \cdot MgSO_4 \cdot 4H_2O(D_2) \rightarrow \text{langbeinite, } K_2SO_4 \cdot 2MgSO_4(D_3) + W$,[↗] in presence of a liquid containing chloride.

Point 8 is reached by all solutions originally in the triangle D₂B8, along curve 9-8, carrying $MgSO_4 \cdot H_2O + D_2$. If they started from triangle B8D₃, D₂ is consumed, and the liquid travels on curve 8-4; at point 4, D₃ changes

to D_4 , in the reaction $L + D_3 \rightarrow B + D_4 + H_2O$.[↗] If the liquid started from IV, it dries up at this point; otherwise D_3 is consumed, and the liquid moves on to point 6, etc. If point 8 is reached by liquids originally in triangle $D_3\delta D_2$, $MgSO_4 \cdot H_2O(B)$ is consumed, and the liquid travels on curve 8-3. Now if the original composition also falls in triangle $\delta D_3 3$, D_2 is entirely consumed while the liquid is still on curve 8-3. It then leaves the curve and crosses the D_3 field to one of its two other boundaries. On either boundary, it must reach point 4, and either dry up there or go on to point 6, etc. If the liquid starts in triangle $D_3\delta D_2$ but not in triangle $\delta D_3 3$, the solution on curve 8-3 reaches point 3, where the reaction is $L + D_2 + D_3 \rightarrow D_4 + H_2O$.[↗] (Point 3 is therefore the analog of P_t of Fig. 12-69, where, in an isobaric ternary system a ternary compound, D , appears upon cooling, by the reaction between two solids, A and C , and the liquid at P_t . In the present case, a condensed isothermal quaternary system, the quaternary compound D_4 appears, with loss of water from the saturated solution, W_t being the analog of T , as a product of the reaction between two solids, D_2 and D_3 , and the liquid at point 3.) Now the liquid dries up if it comes from triangle III; but if it comes from IV, it loses its D_2 and goes on to point 4 as drying-up point. (For all other liquids reaching point 3 *via* curve 83, D_2 is consumed if they originate above, D_3 if they originate below, the line $D_4 3$, the liquid then leaving point 3 for curve 34 or curve 32 accordingly.)

The reactions at other incongruent invariant points are: at point 1, $L + A \rightarrow D + D_2 + H_2O$.[↗] at point 2, $L + D_2 \rightarrow D + D_4 + H_2O$.[↗] at point 5, $L + D \rightarrow D_1 + D_4 + H_2O$.[↗] at point 6, $L + D_4 \rightarrow B + D_1 + H_2O$.[↗]

Between 25° and 55°, there occur a number of condensed invariant points of liquid and four solids, in connection with the appearance and disappearance of the fields of solids stable at one and not at the other of these temperatures. These are determined by intersections of the univariant curves of threefold saturation — those which appear as isothermally invariant points on the isotherms — on plots of various composition variables against temperature, as explained earlier (under Fig. 16-36).

2. Saddle points and quasi-ternary sections are illustrated in Fig. 17-23, the schematic Jänecke diagram of the 25° isotherm of the system Na_2SO_4 - $MgMoO_4$ - H_2O .¹¹ The six solid phases are: A , $Na_2MoO_4 \cdot 2H_2O$; B , $Na_2SO_4 \cdot 10H_2O$; C , $MgSO_4 \cdot 7H_2O$; D , $MgMoO_4 \cdot 5H_2O$; D_1 , astracinite, $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$, congruently soluble; D_2 , $Na_2MoO_4 \cdot MgMoO_4 \cdot 2H_2O$, incongruently soluble. The stable pair is $Na_2SO_4 \cdot 10H_2O + MgMoO_4 \cdot 5H_2O$, but a solution saturated with these two salts alone can-

¹¹ W. F. Linke, *Dissertation*, New York University, New York, 1948.

not be made from the pair and water. Three of the four invariant points, namely 1, 3, 4, are congruently saturated, each lying in the triangle of its three salts; these are points of minimum W_l and represent the congruent drying-up points for solutions in the triangles of corresponding number.

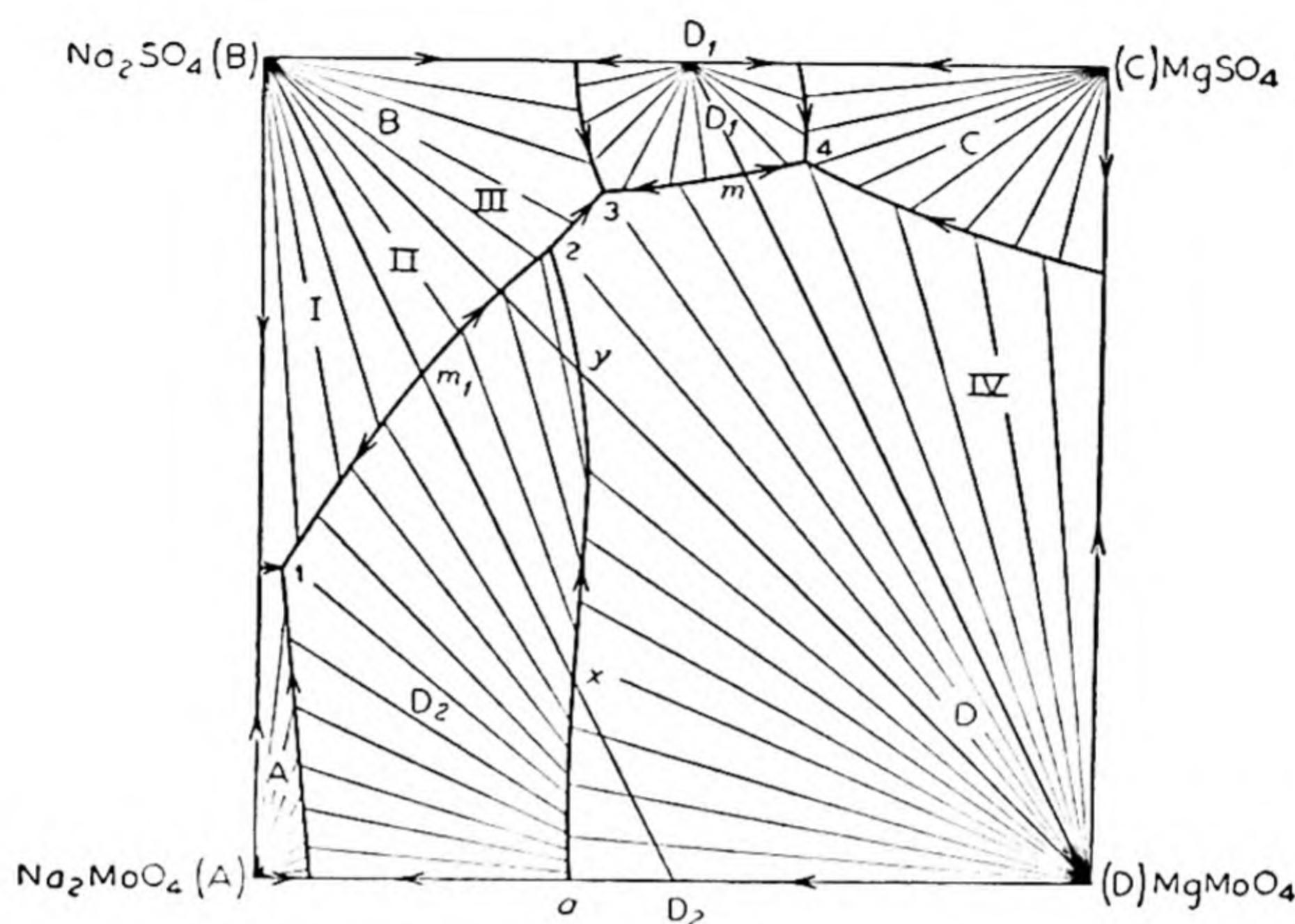


FIG. 17-23. System $\text{Na}_2\text{SO}_4\text{--MgMoO}_4\text{--H}_2\text{O}$, at 25° .

The section D_1D is quasi-ternary, with a saddle point m on the curve 34 . All curves except $a2$ are of even reaction, for precipitation of two salts on evaporation. Curve $a-2$ is odd, for the transition $L + D \rightarrow D_2 + W$. Since the curve $1-2$ represents precipitation of B and D_2 on evaporation, point m_1 , on the line BD_2 , is a saddle point for the curve, a maximum of W_l on it; but the section BD_2 of the isotherm is not quasi-ternary since it is cut by the transition curve.

Curve $a-2$ is reached from the D field by all solutions in the region $a2D$, but the incongruently saturated invariant point 2 is reached only by solutions in the quadrangle $B2DD_2$. Solutions originating in the region axD_2 , therefore, lose all their solid D_2 phase as they travel along the curve before reaching point x ; then, carrying only D_2 as solid phase, they cross the D_2 field to one of the curves leading to point 1 where they dry up congruently to $A + B + D_2$, together with all other solutions in triangle I. Solutions originating in xyD_2 also cross the curve when D is consumed, and finally reach point 2 along curve m_12 .

Liquids reaching point 2, either along curve m_1-2 or along curve $x-2$, undergo the invariant diagonal reaction $L(2) + D_2 \rightarrow B + D + W$. If they originate from triangle II they dry up incongruently at point 2; other-

wise, losing solid D_2 completely, they proceed on curve 23 to dry up congruently at point 3 to $B + D + D_1$.

E. Solid Solution

As in the additive systems of Chapter XVI, the isothermal solubility relations resulting from the formation of solid solution in the saturating salts could all be discussed on the basis of the isobaric or condensed polythermal projections of the schematic freezing point relations of non-aqueous reciprocal systems, in Chapter XV. Again those diagrams apply for the present case by substitution of W_l as the variable in isothermal evaporation for T in the condensed ternary relations.

If the solid solubility of the four salts is complete, the isothermal aqueous solubility surface would be smooth and continuous, with slopes and curvature depending on the relative solubilities of the separate salts and on the degree of non-ideality of their solid solution, fixing the direction of change of W_l . Such a diagram is suggested by Jänecke¹² for the 25° isotherm of the

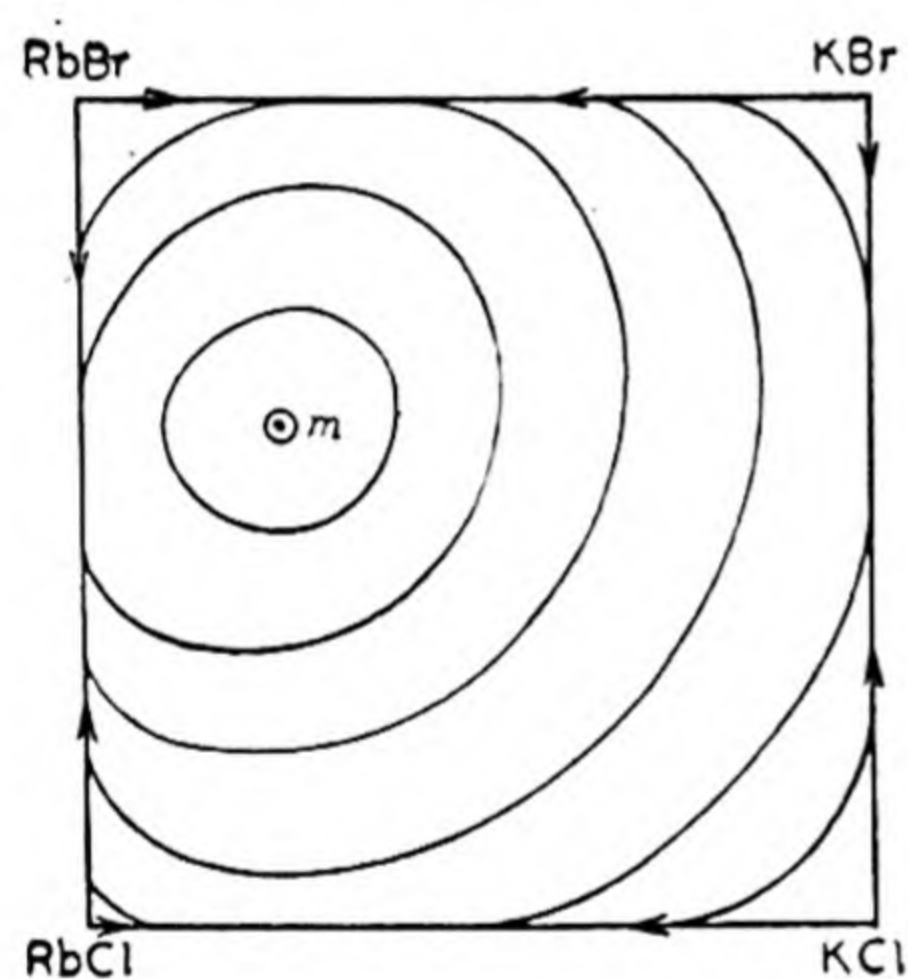


FIG. 17-24. System RbCl-KBr- H_2O , hypothetical.

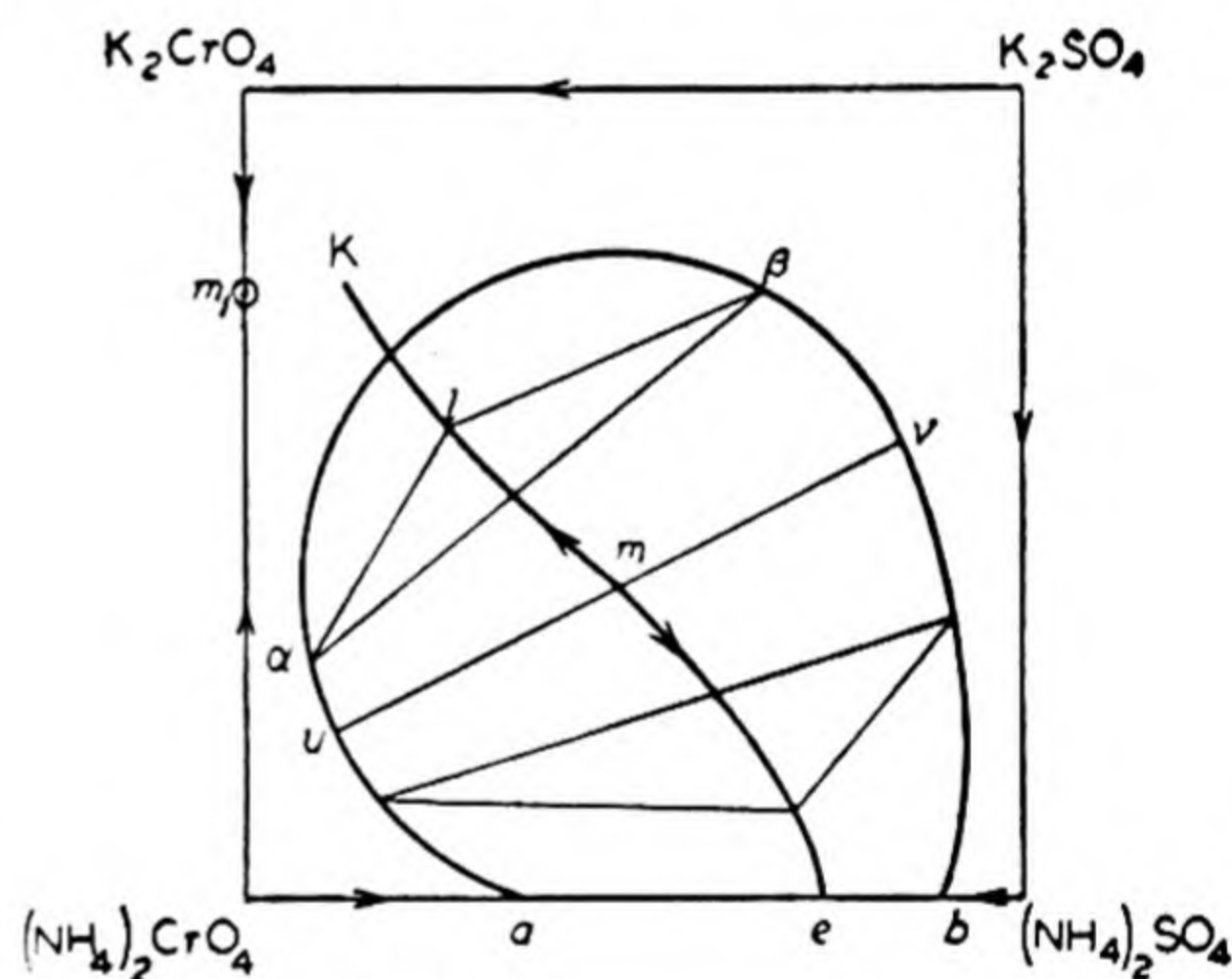


FIG. 17-25. System $(NH_4)_2CrO_4$ - K_2SO_4 - H_2O , hypothetical.

system H_2O -RbCl-KBr (Fig. 17-24). Each ternary system is represented as of the Roozeboom Type II (Fig. 13-25b), with a minimum in W_l for each of the four ternary sides of the square. In this case we may then expect a quaternary minimum at m , which would be the drying-up point of the system for the process of isothermal evaporation with "effective removal of solid." The contours on the diagram are schematic isohydrores.

For the system H_2O -(NH_4) $_2$ CrO $_4$ - K_2 SO $_4$ at 25° Jänecke¹² suggests the diagram of Fig. 17-25. The only pair with limited solid miscibility is $(NH_4)_2$ CrO $_4$ -(NH_4) $_2$ SO $_4$. The curve eK is quaternary liquid saturated with two conjugate solid solutions, each lying on a boundary of the MG , $a\alpha\beta b$.

¹² E. Jänecke, *Z. Elektrochem.*, 43, 924 (1937).

W_i is shown falling continuously from K_2SO_4 to K_2CrO_4 and to $(NH_4)_2SO_4$. The ternary isotherm $(NH_4)_2CrO_4$ – K_2CrO_4 – H_2O is of type II with a minimum, m_1 , in a continuous solubility curve, while the system $(NH_4)_2CrO_4$ – $(NH_4)_2SO_4$ – H_2O ¹³ is of type IV (Fig. 13–26) with a break in the solubility curve at e and a gap in the solid solution between a and b . The curve eK is shown with a maximum of W_i at m , a saddle point on the curve eK . The relations with respect to this maximum, with its colinear equilibrium umv , are analogous to those in Fig. 15–19 for the line umv at the T -maximum of the curve E_1mE_2 . The drying-up points of Fig. 17–25 are therefore m_1 and e . This diagram is, then, for the reciprocal case, the analog of Fig. 11–58 for the additive case. Fig. 11–58 may be read as the solubility isotherm of a quaternary system of water and three salts with common ion forming solid solution with a miscibility gap in only one binary combination. Since Fig. 11–58 was originally drawn for ternary boiling point relations, however, the arrows in it must now be interpreted as indicating the direction of increasing water content, as the analog of the original temperature variable.

F. Note on the Word “Congruent”

The word “congruent” has been used in such a variety of connections, that it is important to summarize its applications.

1. Binary Systems

If the 2-phase equilibrium of melting or vaporization of a solid binary compound, C , involves phases of the same composition, over a range of T and P , it is called a *congruent transition*. The 3-phase singular point for the equilibrium LCV, with $C = L$ in composition, is the *congruent melting point* of the compound; the similar equilibrium LCV, with $C = V$ in composition, is the *congruent sublimation point* of the compound. The 4-phase invariant equilibrium ACLV, A being a second solid, and all four phases differing in composition, is the *incongruent melting point* of the compound.

In connection with binary compounds we have also distinguished as “incongruent” the eutectic equilibrium in which the order of phases is ALCV in contrast to the “congruent order” ALVC.

2. Ternary Systems; isobaric (or condensed) T/c relations

a. A compound, binary or ternary, may now be congruently or incongruently soluble in the component considered the solvent, such as W , at a particular temperature. It is *congruently soluble* if the line joining W and the composition of the compound cuts the isothermal solubility curve of

¹³ I. C. T., IV–328.

the compound. The point of intersection is then the stable solubility of the compound in pure W, and it marks a maximum of W_1 on the curve.

b. A ternary compound may have a *congruent melting point* (compound with open maximum), if it melts to a liquid of the same composition; this occurs at a 3-phase singular point. It may, on the other hand, melt semi-congruently to a liquid and one other solid, at a 4-phase singular point, with vapor present, or incongruently to a liquid and two other solids at a 5-phase invariant point.

c. A liquid of a condensed invariant point ($L + 3$ solids) is (1) *congruently saturated* with respect to its three solids if L is the interior phase of the composition triangle of the solids; or (2) *incongruently saturated* with respect to its three solids if L is outside the triangle of the solids. In (1) it is a eutectic point, a congruent *solidification end-point* on cooling and a temperature minimum. In (2) it is a peritectic or transition point, the *incongruent solidification end-point* for certain compositions, namely, those falling within the triangle of its solids, and it is not a temperature minimum.

d. With reference to isothermal evaporation of aqueous salt systems, an isothermally invariant solution ($L + 2$ solids) is (1) *congruently saturated* with its two solids if its salt proportions represent a mixture of the two saturating salts, and (2) otherwise *incongruently saturated* with its two solids. In (1) it is a *congruent drying-up point* or *congruent crystallization end-point*, and represents a point of minimum W_1 ; in (2) it is a transition point, it may be the *incongruent drying-up point* for certain compositions, and it is not a minimum in W_1 .

3. Quaternary Systems (condensed isotherms of $W + \text{salts}$)

a. A ternary salt compound (tetragene, hydrated or not, such as kainite, D_4 in Fig. 17-22) may or may not be congruently soluble in water. If the line from W to the compound passes through its solubility surface, or if the compound falls inside its crystallization field in the Jänecke diagram, it is *congruently soluble*, it has a stable solubility in pure water, and this point on its solubility surface marks a maximum in W_1 .

b. An invariant solution is *congruently saturated* with its three solids if its salt proportions represent a mixture of the three solids; it is then a point of minimum W_1 , and a *congruent drying-up point* in isothermal evaporation. It is otherwise *incongruently saturated*, a transition point, and only an *incongruent drying-up point*.

c. A pair of solids is *congruently soluble as a pair* if the saturated solution $L + S_1 + S_2$ can be prepared from water and the two solids. The liquid, *congruently saturated* with the two solids, represents a maximum in W_1 (saddle point) on a curve of twofold saturation, where it is cut by the plane WS_1S_2 .

Chapter XVIII Aqueous Quinary Systems

Introductory; Types

For every additional component another variable has to be sacrificed for the sake of some representation of the equilibrium relations in a given number of dimensions. In quaternary systems, with three independent composition terms, a complete isobaric isotherm requires a 3-dimensional figure; and by sacrificing the indication of water content we may represent, on a plane (polyhydric) projection, the salt proportions of saturated solutions. The projection of this essential information requires a 3-dimensional model for a quinary system. The neglect, however, of the concentration of one of the components is a satisfactory procedure in general only for aqueous salt systems, in which the role of the component water is distinctly different from that of a salt, and in which the primary interest is usually in isothermal relations and in the interrelation of a few isotherms. A system such as one of five metals, or in general of five comparable components, would involve greater difficulty in its representation, particularly since the primary interest may be in the temperature variable. We restrict ourselves, therefore, to **aqueous salt systems**, the important **types** being the following:

A. Water + four salts with a common ion (additive system), with no hydrolysis.

B. Water + a reciprocal salt pair + one of the acids or bases of this salt pair, in excess. The system contains, in other words, two acids and two bases without the restriction that the sum of the acid equivalents equals the sum of the base equivalents. (Analytically a salt is simply an equivalent combination of acid and base.)

C. Water + two acids (or bases) and three bases (or acids) with the restriction that the sum of the acid equivalents equals the sum of the base equivalents. More commonly expressed as a system of water + six salts containing two ions of one sign and three of another, this is the usual quinary aqueous system of reciprocal salts. Hydrolysis is assumed absent.

Disregarding the water content of the saturated solutions, we may represent the proportions of the salts in the saturated solutions, at constant pressure and temperature, in a 3-dimensional "polyhydric" projection.

The number and forms of the plane faces of this model will depend upon the number and types of the quaternary systems making up the five-component system, for each face will be a quaternary polyhydric projection (Jänecke diagram) of the type of Fig. 16-18 or 17-7.

A. Type A: Additive Quinary System

1. Schematic Diagrams

In the system of water + four salts with a common ion, there are four quaternary systems of water and three salts with a common ion, and the polyhydric isothermal space model for saturated solutions will therefore be a regular tetrahedron (Fig. 18-1). Each face is the Jänecke diagram of the salt proportions in the saturated solutions of a quaternary isotherm (Fig. 16-18), and the whole figure is the analog of Fig. 16-10. We note again, in other words, the analogy between the variable of temperature in an isobaric diagram, with that of "water content" (strictly the vapor pressure) in the condensed isotherm of an aqueous salt system of next higher order. Hence the polythermal projection of a quaternary isobar (Fig. 16-10) shows the same schematic relations as the polyhydric projection of this condensed quinary isotherm (Fig. 18-1). Since only the proportions of four salts are represented, the plotting is exactly the same as in Fig. 16-10.

The four spaces in Fig. 18-1 represent the proportions of salts in quinary solutions saturated with a single salt; the six interior surfaces represent solutions saturated with two salts; the four curves entering the tetrahedron, or the intersections of the surfaces, represent solutions saturated with three salts; and the intersection of these curves, point Q, is the condensed isothermally invariant solution saturated with all four salts. This is the point of minimum "water content" of the isotherm and is the analog of the quaternary eutectic of Fig. 16-10, the solid phases in both cases being assumed to be pure components. The process of isothermal evaporation is followed exactly as the process of cooling is followed in Fig. 16-10, the withdrawal of water from the present system being analogous to the with-

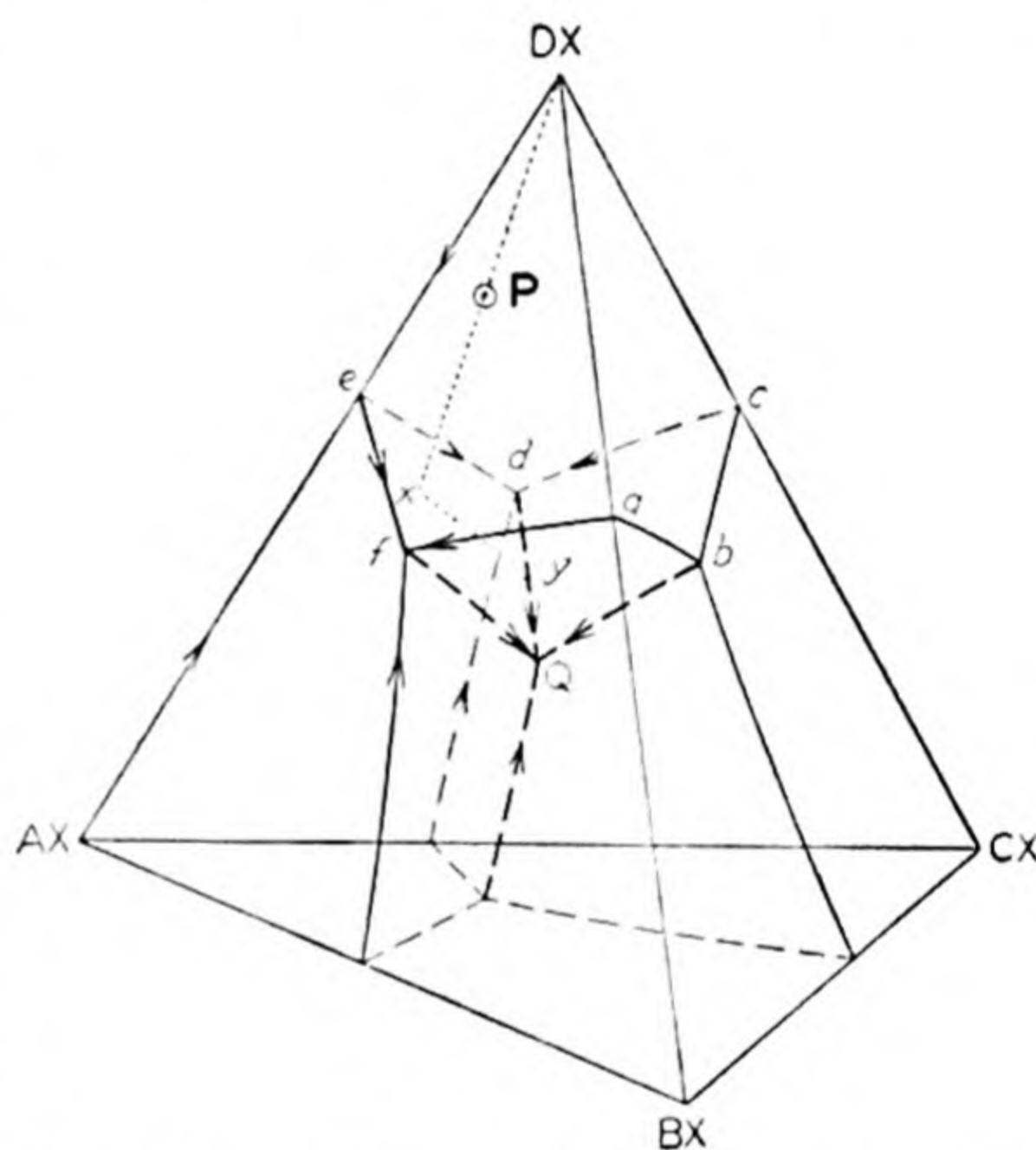


FIG. 18-1. Quinary isotherm, showing salt proportions of saturated solutions.

drawal of heat in that figure. An unsaturated solution **P**, with salt proportions falling in the uppermost volume, begins to precipitate **DX** upon isothermal evaporation when it becomes saturated, that is, when the isohydric surface, the analog of the isothermal surface 123 of Fig. 16-9(f), reaches the point **P**. As **DX** is precipitated, the composition of the liquid (in salt proportions) changes on the line **DX-P** until it reaches the surface for saturation with both **DX** and **AX**, at point *x*. With removal of both **DX** and **AX**, the solution follows a course on this surface fixed by the plane **AX-P-DX**, until it reaches one of the curves, in this case the curve *dQ*, for saturation with **DX + AX + CX**, at point *y*. Then, precipitating these three salts, the solution moves to the invariant point **Q**, where it dries up to leave a mixture of the four salts in the proportions **P**. If tables or contours are available, giving the water content at the various points in the course followed by the liquid composition, it is possible to make calculations of the relative amounts of the phases during the process, through the use of sections and projections of the relations, as stated in connection with Fig. 16-10.

All this requires a 3-dimensional model which is merely *pictured* in Fig. 18-1. A partial representation on a plane is possible by the orthogonal projection on the base, of all points and curves involving saturation with one

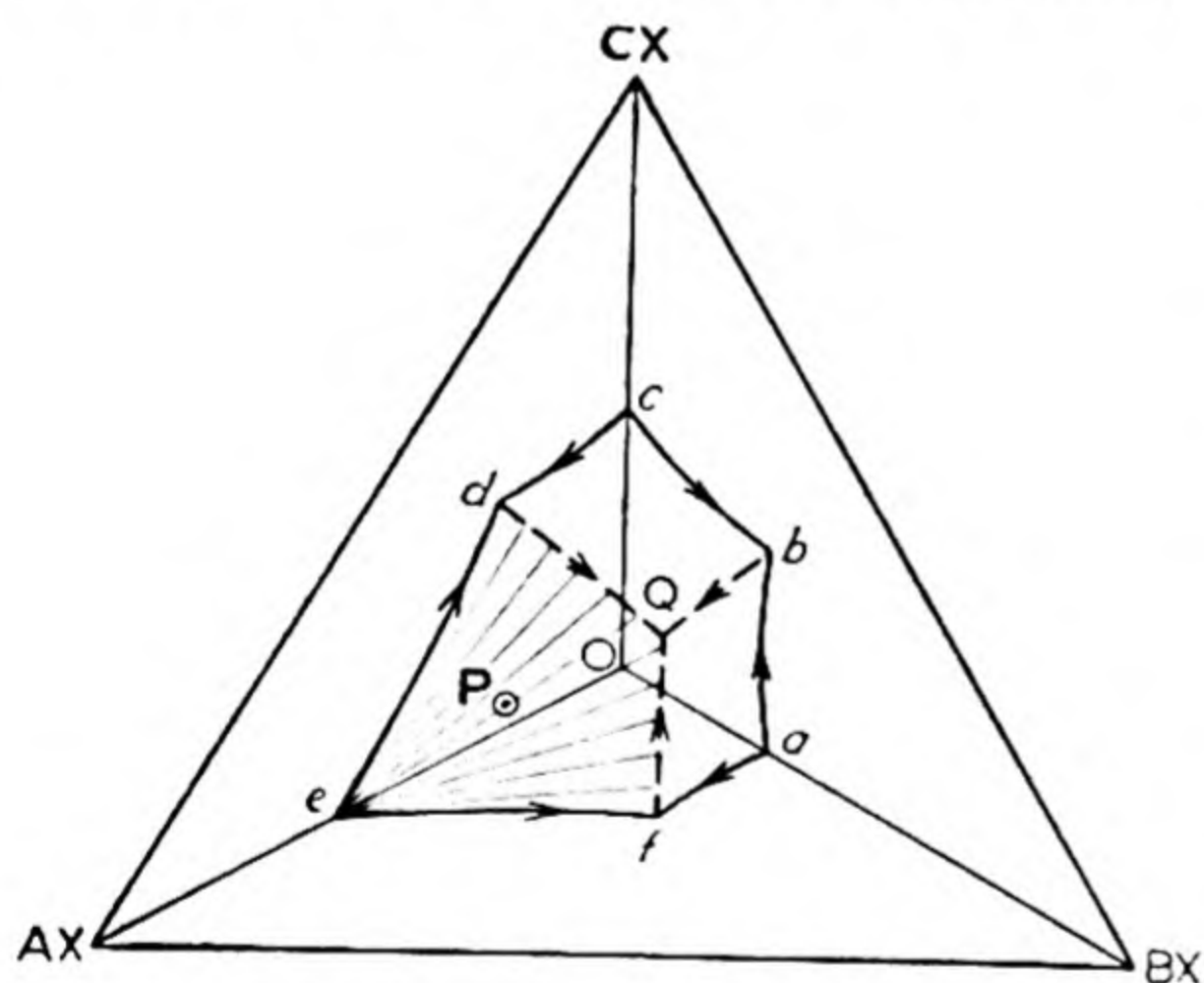


FIG. 18-2. Orthogonal projection of surfaces for saturation with two salts (**DX** in common).

common specified salt, say **DX**, together with one or more other salts (Fig. 18-2). This figure is an orthogonal projection of the surfaces bounded by *abcdef*, upon the face **AX-BX-CX**. There are three fields, each representing quinary solutions saturated with two salts, one of which is **DX**. The points *e*, *a*, and *c* are ternary solutions saturated with **DX + AX**, **BX**, and **CX** respectively; points *b*, *d*, and *f* are quaternary solutions saturated with three salts; the curves *bQ*, *dQ*, and *fQ* are quinary solutions of threefold saturation; and **Q** is the quinary invariant solution saturated with four salts. Such a diagram, of course, shows only part of the relations, since those relations lying below the three surfaces here projected are not included at all. The diagram may be plotted as explained for Figs. 16-2 and 16-13; the percentages of the three salts **AX**, **BX**, and **CX**, in total salts (water neglected), may be plotted directly in the triangle **AX-BX-CX**, after adding to each one third the percentage of **DX**.

The usual diagram plotted for saturation with a common salt, however, is very similar to Fig. 18-2, but not related to the finite tetrahedron of Fig. 18-1. It is rather the analog of the Löwenherz diagram of Figs. 16-8 and 16-20, and is shown in Fig. 18-3. The three axes, intersecting at 120° , are used to plot the number of moles of each of the three salts indicated, per 1000 grams or moles of water, in the saturated solution. This permits direct plotting of the data, and the concentration of the common saturating salt is tabulated together with information on the water content. Figs. 18-2

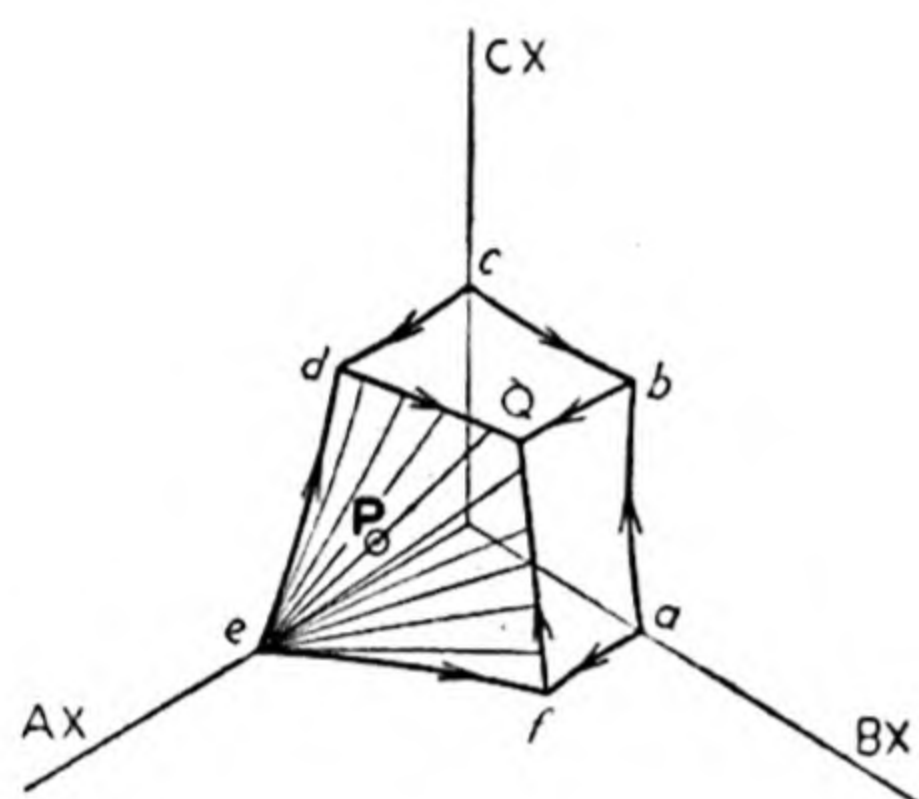


FIG. 18-3. Löwenherz type of diagram, for saturation with DX in common.

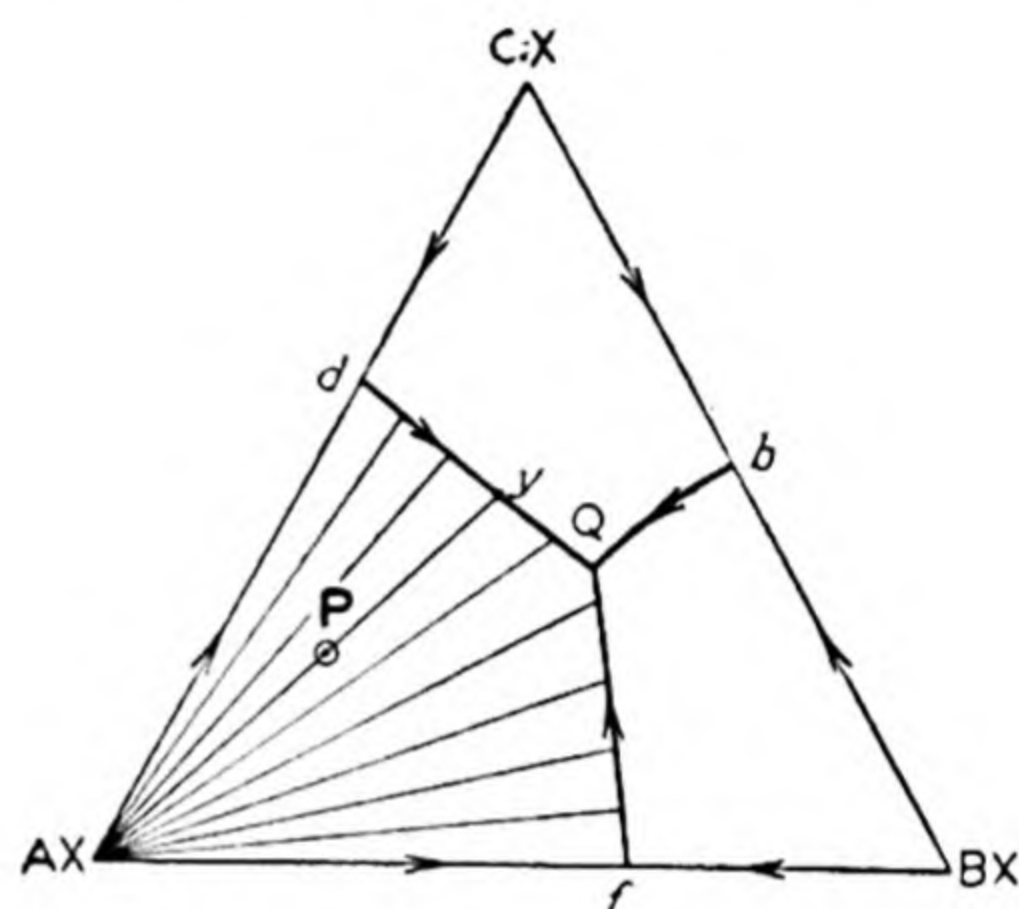


FIG. 18-4. Jänecke diagram for saturation with DX in common.

and 18-3 have the limitations and disadvantages already discussed in connection with their analogs (Figs. 16-13 and 16-20). A quinary point cannot be interpreted without first transforming effectively into a perspective projection; and the crystallization paths are curved. In more complex systems, therefore, these projections are not sufficient to fix the direction of falling "water content" along interior quinary curves of threefold saturation, or to establish whether a particular invariant point (liquid + 4 salts) is congruently or incongruently saturated. Hence, although a great deal of work is represented directly according to the method of Fig. 18-3, it will be more convenient for certain purposes to use the Jänecke projection (perspective or radial) of the same relations (Fig. 18-4). This is a perspective projection of the relations already shown in Figs. 18-2 and 18-3, from the DX corner to the opposite face of the tetrahedron. It disregards, that is, both the water content and the concentration of the salt DX, to show the proportions of the three salts AX, BX, and CX among themselves, in solutions saturated with DX and other salts.

The units involved in Figs. 18-1 to 18-4 will be illustrated with specific values. If a quinary solution contains 13.64% AX, 2.27% BX, 6.82% CX, 31.82% DX, and the rest (45.45%) H_2O , then Fig. 18-1 represents the values 25% AX, 4.2% BX, 12.5% CX, and 58.3% DX, the relative per-

centages of dissolved salts. The orthogonal projection (Fig. 18-2) represents $(25 + 58.3/3)$ or 44.4% AX, $(4.2 + 19.4)\%$ BX, and $(12.5 + 19.4)\%$ CX. The Löwenherz diagram (Fig. 18-3) represents 30 units for AX, 5 for BX, and 15 for CX, as grams of each salt per 100 grams of water, the total weight of salts (including DX) being 120 per 100 of water. The Jänecke diagram (Fig. 18-4) represents 60% AX, 10% BX, and 30% CX, since both DX and H₂O are here disregarded.

The relation between Fig. 18-2 and Fig. 18-4 is that explained in Chapter XVI for the orthogonal and Jänecke diagrams of additive quaternary systems, with %W in place of %DX among the salts. But it must also be noted that in the present orthogonal diagram (Fig. 18-2) the usual "tie-lines" may not be shown, since the corners represent not the salts but their saturated solutions.

In Fig. 18-4 the crystallization paths are straight lines radiating from the point representing the salt composition of the particular solid phase. A solution P, on evaporation, is presumed to have become saturated first with DX, and to reach the surface of saturation with AX + DX. Since DX is not plotted in the diagram, the point P still represents the original composition of the solution, in respect to the proportions of the salts AX, BX, and CX, despite separation of DX; or, this projection superimposes the points P and *x* of Fig. 18-1. Hence when the surface of twofold saturation is reached, and AX begins to separate together with DX, the composition of the liquid proceeds away from AX on a straight line through P. When it reaches curve *dQ*, it must travel toward Q, away from the side AX-CX while precipitating the salts AX and CX in addition to DX. Such diagrams therefore serve to fix the direction of isothermal evaporation and hence of falling "water content," on the curves of threefold saturation. An invariant point like Q, in a tetrahedron like Fig. 18-1, is congruently saturated with its four salts if it lies inside the sub-tetrahedron defined by these salts. This can be determined by considering, when necessary, two such perspective projections both including the same invariant point.

2. Example; Double Salts

For an example of a quinary isotherm with double salts, we shall consider the system NaCl-Na₂SO₄-Na₂CO₃-NaHCO₃-H₂O at 20°,¹ with the solid phases A, Na₂CO₃·10H₂O; B, Na₂SO₄; B', Na₂SO₄·10H₂O; C, NaHCO₃; D, burkeite, or Na₂CO₃·2Na₂SO₄; E, trona, or Na₂CO₃·NaHCO₃·2H₂O; and F, NaCl. Fig. 18-5 shows the isothermal relations, the tetrahedron

¹ J. E. Teeple, *Industrial Development of Searles Lake Brines*, Chem. Catalog Co., N.Y., 1929, p. 162. The schematic tetrahedron of Fig. 18-5 is sketched from the projections of Figs. 18-9 and 18-10, which come from Teeple's book.

representing the proportions of the four salts in saturated solutions. The four faces of this tetrahedron are the quaternary isotherms (Jänecke diagrams) of Fig. 18-6^{1a}. The directions of falling W_i on quinary curves, for

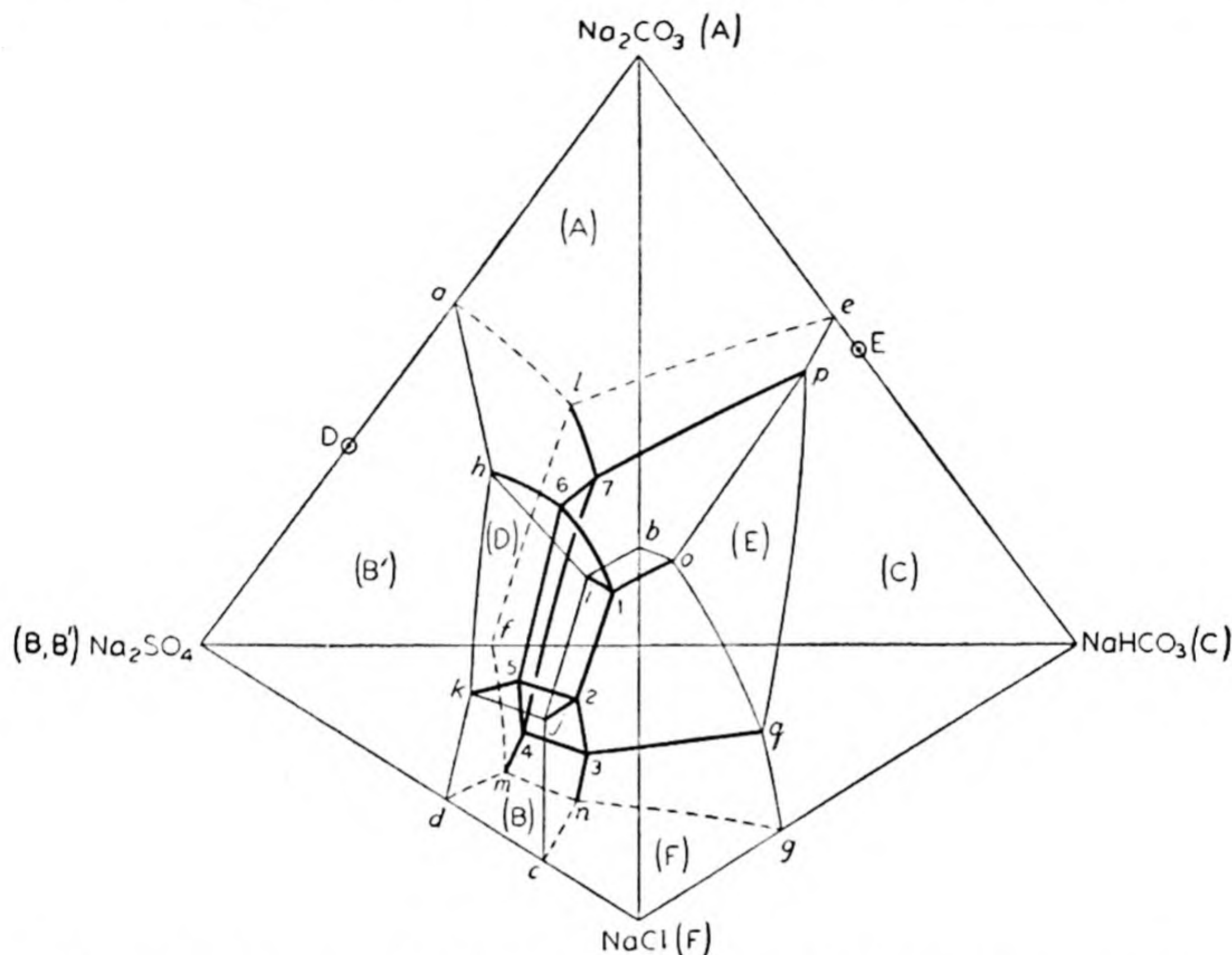


FIG. 18-5. System $\text{NaCl-Na}_2\text{SO}_4\text{-Na}_2\text{CO}_3\text{-NaHCO}_3\text{-H}_2\text{O}$, at 20° .

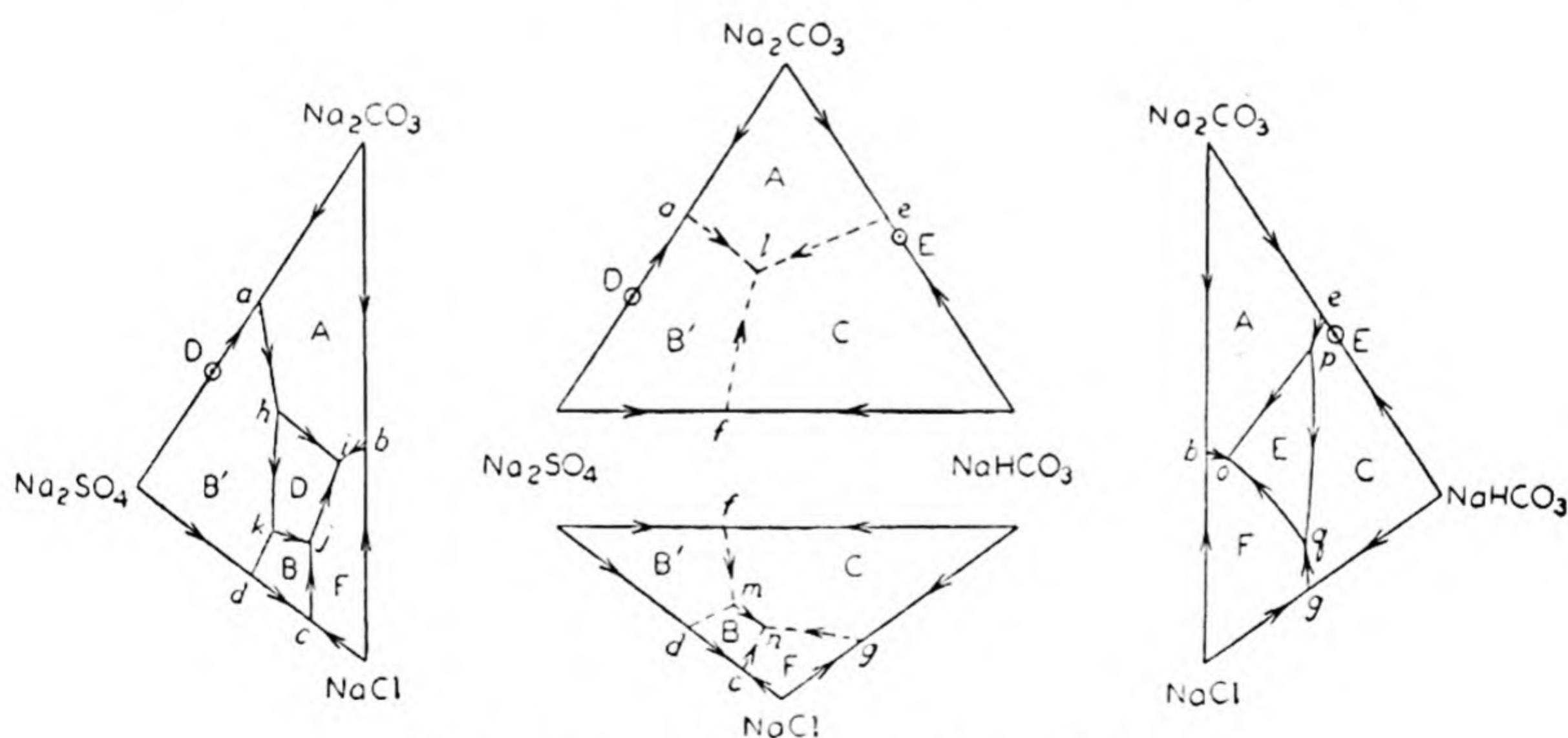


FIG. 18-6. The faces of Fig. 18-5.

the course of isothermal evaporation, are: $l \rightarrow 7$, $p \rightarrow 7$, $7 \rightarrow 6$, $7 \rightarrow 4$, $h \rightarrow 6$, $6 \rightarrow 5$, $6 \rightarrow 1$, $q \rightarrow 3$, $n \rightarrow 3$, $4 \rightarrow 3$, $3 \rightarrow 2$, $j \rightarrow 2$, $5 \rightarrow 2$, $2 \rightarrow 1$, $o \rightarrow 1$, $i \rightarrow 1$. With seven solids, there are seven spaces in the tetrahedron. The diagram is

^{1a} The face ABF is the Jänecke diagram of the system $\text{NaCl-Na}_2\text{SO}_4\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$ at 20° discussed as Fig. 16-35.

schematic, and the dimensions have been somewhat distorted for the sake of clarity. The only space not easily visualized is that for saturation with the double salt E, which is therefore shown separately in Fig. 18-7.

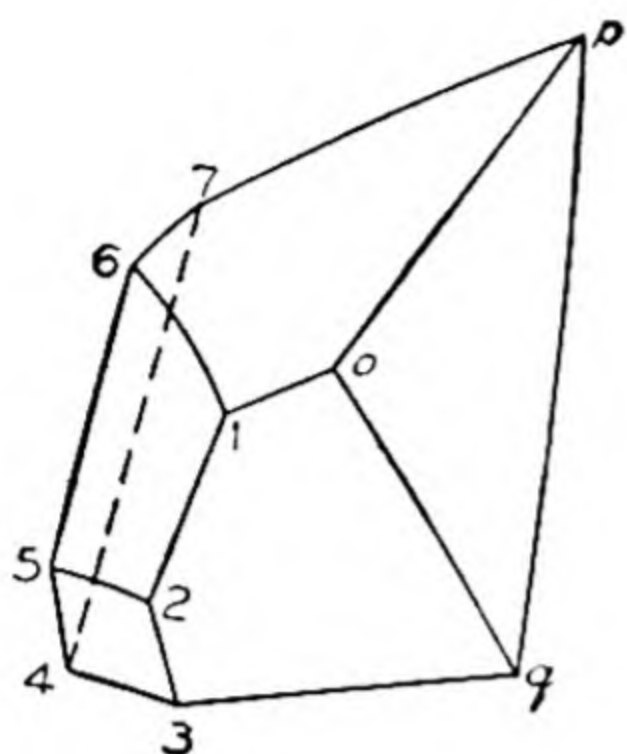


FIG. 18-7. The space for saturation with the solid phase E (trona), or $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$.

There are seven 4-salt invariant points.

For points 1, 2, and 3, the four salts define the three sub-tetrahedra I, II, and III, respectively, of Fig. 18-8. All quinary solutions must dry up to one of these three combinations, since these sub-tetrahedra comprise the whole. All three invariant points, as will be seen below from Fig. 18-11, fall in tetrahedron I. Hence point 3, saturated with the salts of III, is the incongruent drying-up point

for all solutions with original compositions (salt proportions) in III, with the reaction $\text{L} + \text{C} \rightarrow \text{B} + \text{E} + \text{F} + \text{W}$.[↗] Point 2, falling in I, is the incongruent drying-up point for solutions in II, in the reaction $\text{L} + \text{B} \rightarrow \text{D} + \text{E} + \text{F} + \text{W}$.[↗] Point 1, falling in I, is the congruent drying-up point for its

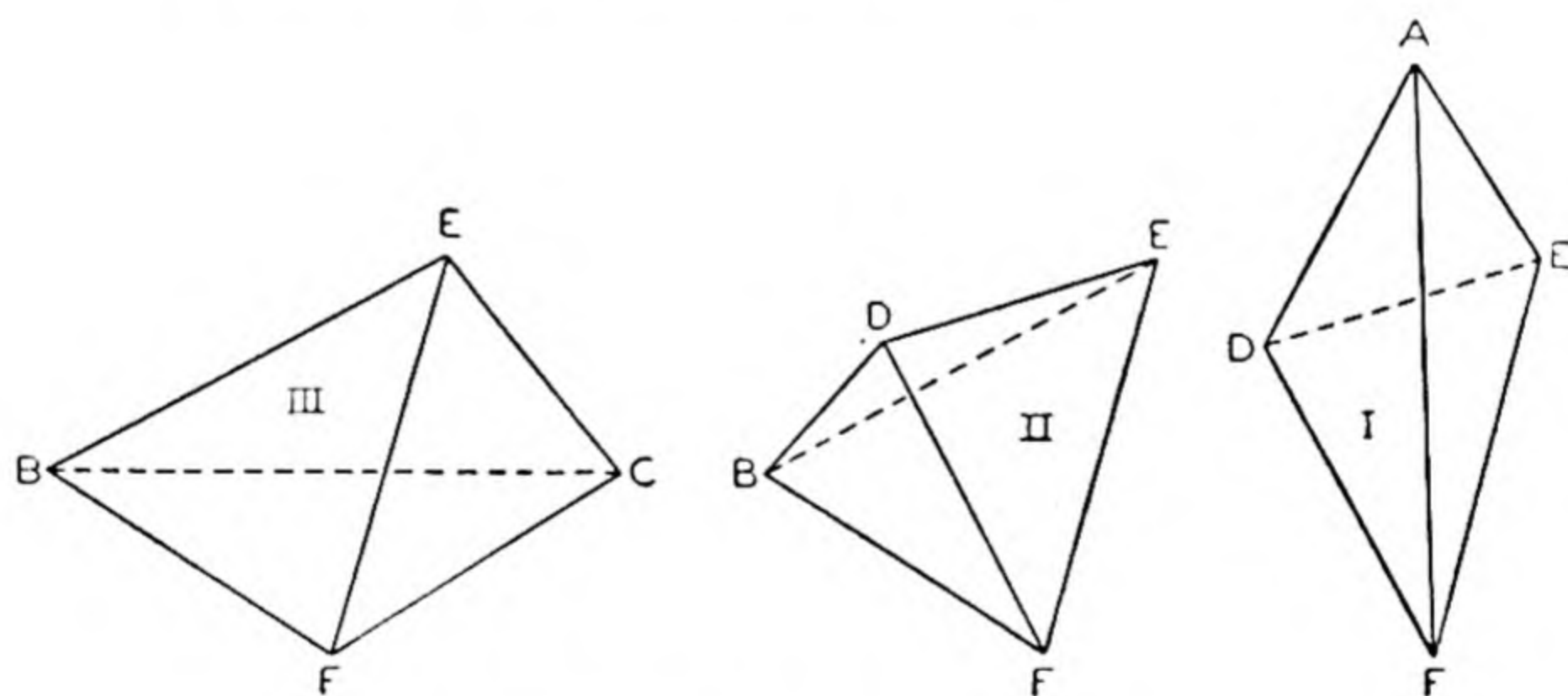


FIG. 18-8. The sub-tetrahedra of Fig. 18-5.

tetrahedron, and is the W_t -minimum of the isotherm; its reaction is

$\text{L} \rightarrow \text{A} + \text{D} + \text{E} + \text{F} + \text{W}$.[↗] For the four remaining invariant points (4-7), the four salts saturating the solutions describe planes on the faces of the tetrahedron (never involving F or NaCl), so that they are only transition points and never drying-up points. Their phase reactions are in fact of the type in which the liquid phase is inevaporable, not only invariant in composition but also constant in actual quantity (equilibria of lower order). At point 7, the reaction is $\text{A} + \text{C} \rightarrow \text{E} + \text{W}$,[↗] in presence of a liquid

containing chloride and sulfate, and saturated with B' . At point 6, $A + B' \rightarrow D + W$,[↗] in presence of a liquid containing chloride and bicarbonate, and saturated with E. The reaction at both point 5 and point 4 is simply the dehydration $B' \rightarrow B + W$,[↗] in presence of solution containing carbonate, bicarbonate and chloride, and saturated with the pairs $D + E$ and $C + E$ respectively. Besides the liquid, these various non-reacting saturating solids also remain unchanged in quantity during the invariant reactions at the points 7, 6, 5, 4.

The points 5 and 4 are in fact simply parts of the isopiestic "dehydration surface" *dk54m* of Fig. 18-5, for the reaction $B' \rightarrow B + W$.[↗] This surface represents solutions in equilibrium with the two solids $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(B')$ and $\text{Na}_2\text{SO}_4(B)$. It is the quinary analog of the "dehydration curves" discussed in Chapter XVI, Section E. Liquids reaching this surface or any of its boundary curves, whether "quaternary" or "quinary," become invariant, both in composition and in quantity, since in respect to the reaction $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$,[↗] the system, in three condensed phases, is ternary. The surface itself is reached from the B' space, by liquids precipitating the hydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. These approach the surface on a straight line path from the Na_2SO_4 corner; they stop on the surface, without traveling on it, while the hydrate is transformed to anhydrous $\text{Na}_2\text{SO}_4(B)$, and then cross the surface into the B space. The curves *m4*, *45*, and *5k* are reached by liquids carrying the hydrate together with a second solid. Thus the curve *m4* is reached by liquids originating in the space *BfCm4*, traveling on the section *fm4* of the surface *lfm47*, precipitating $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and NaHCO_3 . These stop, invariantly, on the curve *m4*, while the hydrate is dehydrated, and then travel on the surface *m43n*, for saturation with $\text{Na}_2\text{SO}_4 + \text{NaHCO}_3$.

Fig. 18-9 is the diagram (according to the method of Fig. 18-3) of the surfaces of solutions saturated with $\text{NaCl}(F)$ as a common phase. It may be said to be somewhat like a projection, similar to an orthogonal projection, of the surfaces bounded by *boqgneci*, from the NaCl corner upon the opposite face. It is plotted, however, in the manner of a Löwenherz diagram, in moles of salt per 1000 moles of water. The field marked C, therefore, represents solutions saturated with both NaCl and NaHCO_3 . The crystallization paths are curves, radiating, for the A, B, and C fields, from the points *b*, *c*, and *g*, respectively. The quinary curves *j2* and *q3* are curves of "odd" reaction, $B-$, $D+$, $F+$ on *j2* and $C-$, $E+$, $F+$ on *q3*; these reactions are deduced on the basis of the prospective projection in Fig. 18-11. The crystallization paths in the D field then radiate from some point outside the

field, fixed by extrapolating the curve ij back to a line, drawn from the origin of the axes, representing the proportions of Na_2CO_3 and Na_2SO_4 in burkeite (D), namely, point y . In similar fashion, point x is the origin of the crystallization paths for the E field.

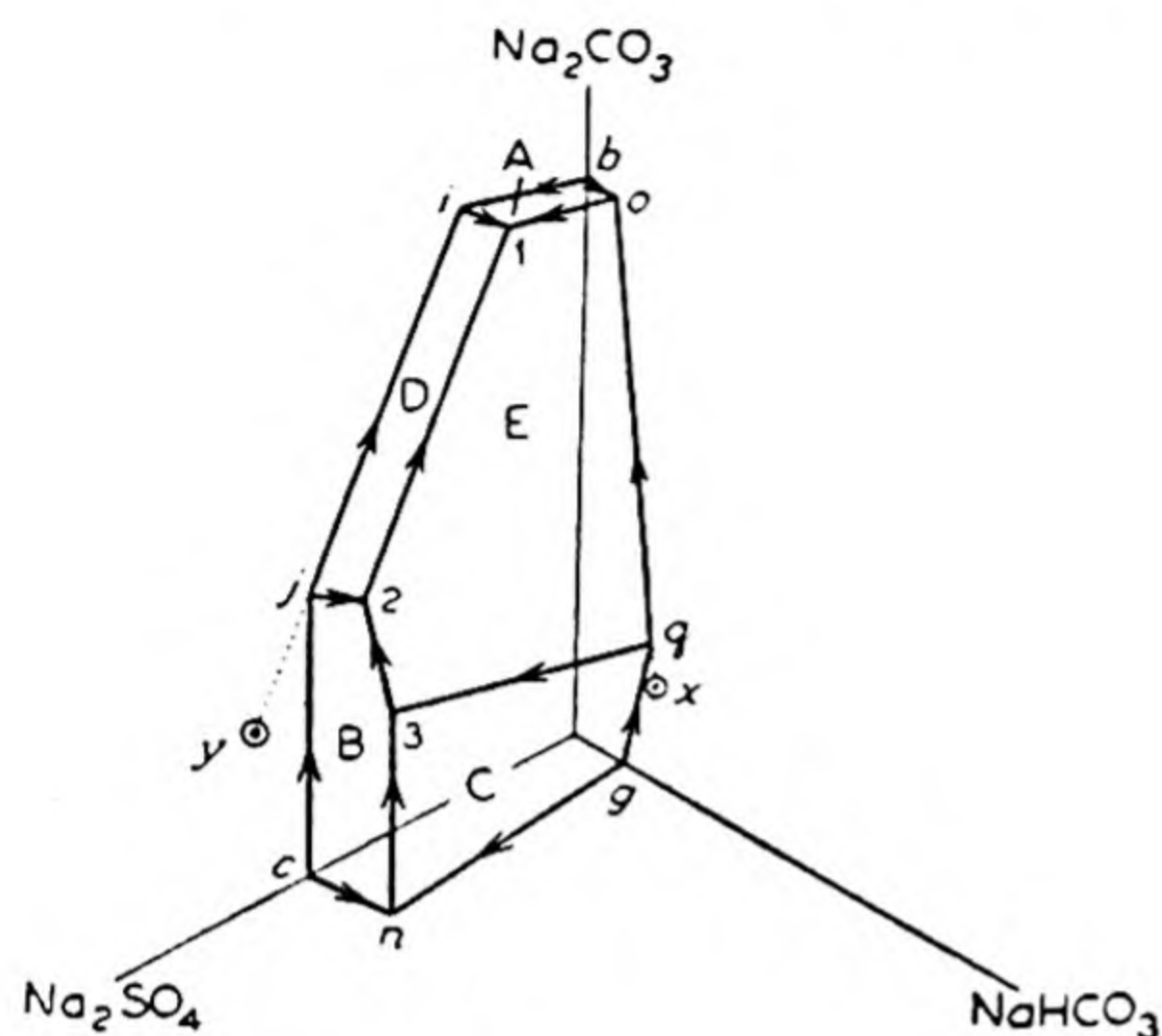


FIG. 18-9. Solutions saturated with NaCl in common, according to method of Fig. 18-3.

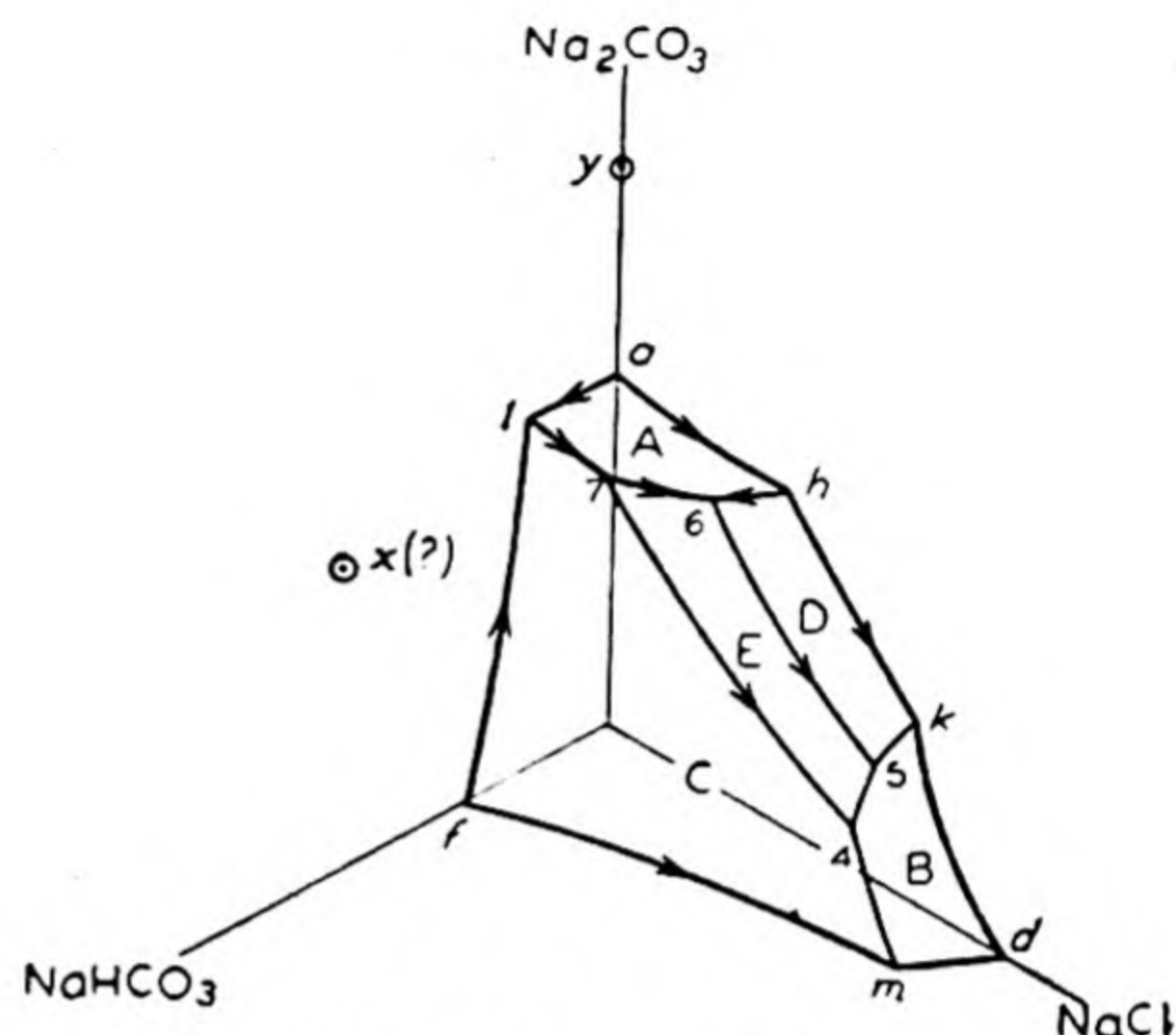


FIG. 18-10. Solutions saturated with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in common, according to method of Fig. 18-3.

Fig. 18-10 is a similar view into the tetrahedron, from the Na_2SO_4 corner, and represents solutions saturated with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in addition to the salts marked in the various fields. No arrows are placed on the boundaries of the field for saturation with $B + B'$, since these curves are not traveled by solution during isothermal evaporation at equilibrium.

Figs. 18-11 and 18-12 are the perspective (Jänecke) diagrams for the relations shown in Figs. 18-9 and 18-10 respectively; Fig. 18-11 for common saturation with NaCl, and Fig. 18-12 for common saturation with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Now all the crystallization paths are straight lines, and the points of origin may be fixed without extrapolation even for the D and E fields. No crystallization paths are drawn for the B field of Fig. 18-12, since, as explained above, this surface (saturation with B and B') is not traveled. Since these are perspective projections, the points A and D are superimposed in Fig. 18-12.

The course of isothermal evaporation of solutions saturated with NaCl is easily followed on Fig. 18-11. Point 3 is reached by all solutions falling in the quadrangle $B3EC$, and those originating in the triangle BEC dry up, incongruently, at point 3, to leave $F + B + E + C$. Point 2 is reached from the quadrangle $BD2E$, and solutions in triangle BDE dry up at point 2 to leave $F + B + D + E$. Point 1 is the congruent drying-up point for solutions in triangle DAE , which leave $F + D + A + E$. Curves $j2$ and

$q3$ are transition curves and are crossed by liquids in the triangles $Dj2$ and $Eq3$, respectively.

In Fig. 18-12, the invariant point 7 is reached by all solutions originally in the triangle $A7C$, carrying A , C , and B' , on curve $l7$; those coming from the triangle $A7E$ lose solid C at point 7, and then travel on the curve 76 , carrying A , E , and B' , while all others lose A and travel on curve 74 , with C , E , and B' . Point 6 is reached only by solutions in the triangle $A6E$, and

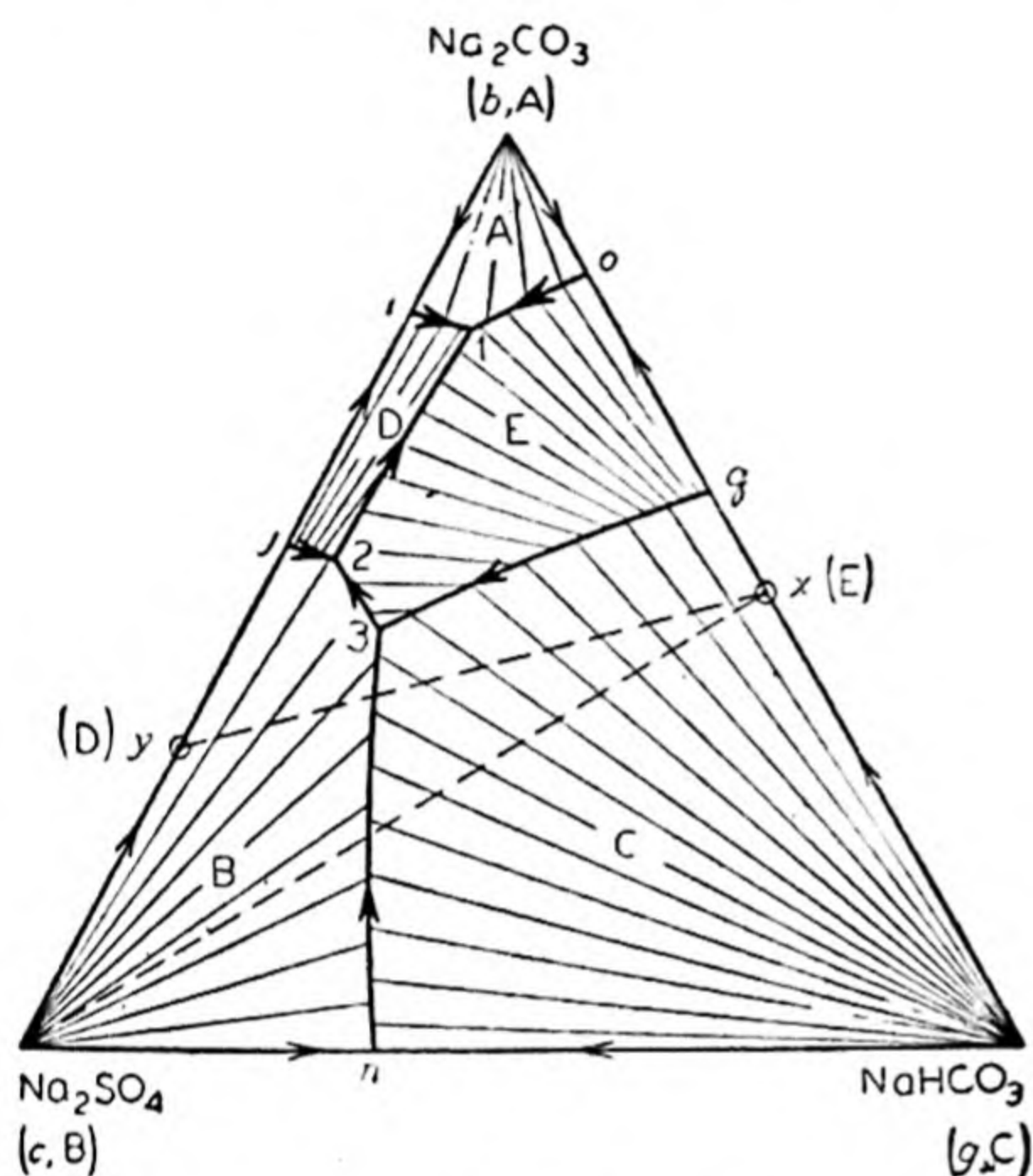


FIG. 18-11. Jänecke diagram of Fig. 18-9.

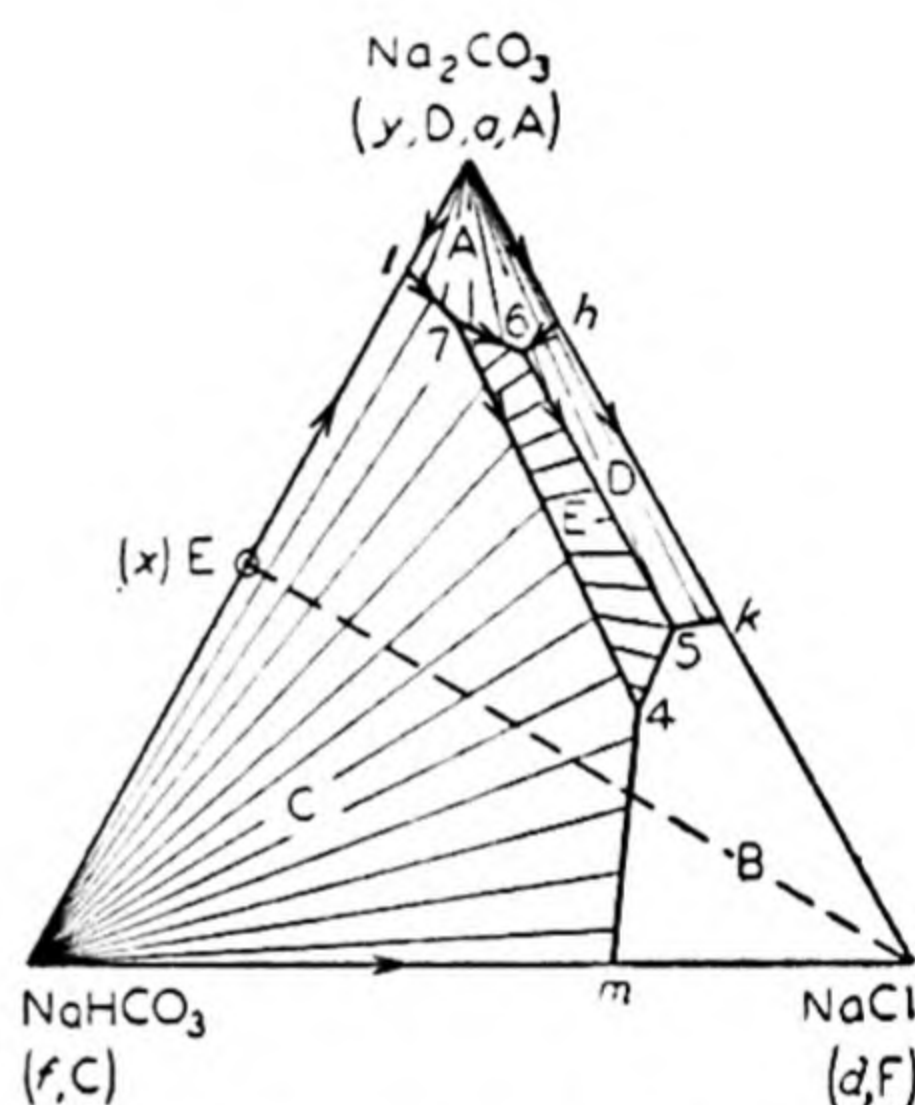


FIG. 18-12. Jänecke diagram of Fig. 18-10.

hence only by solutions in sub-tetrahedra I and II of Fig. 18-8. Fig. 18-12 does not distinguish between these two regions, but the triangle CEF is the projection of III, and it is clear that such solutions cannot reach point 6 since they travel on curve 74 to reach point 4 in every case; (curve 74 is crossed only by solutions in triangle $E74$). At point 6, solutions from II lose A and travel on the curve 65 carrying D , E , and B' , while solutions from I lose B' and proceed on the curve 61 of Fig. 18-5, carrying A , D , and E , to end at the congruent drying-up point number 1. The invariant point 4 is reached from the region $E4C$; at point 4, B' changes to B and the liquid travels on curve 43 of Fig. 18-5, carrying B , C , and E . Point 5 is reached from region $D5E$; again B' changes to B , and now the liquid travels on curve 52 of Fig. 18-5, carrying B , D , and E .

B. Type B

This type, the quinary system of water with two acids and two bases in non-stoichiometric *total* proportions, is mentioned because an example is the

ammonia-soda process for the production of NaHCO_3 . This system consists of water, NaCl , NH_3 , and CO_2 . If NH_3 and CO_2 were present in equimolar proportions, it would be a quaternary system, represented isothermally by Fig. 17-18 as the system $\text{NaHCO}_3\text{--NH}_4\text{Cl--H}_2\text{O}$ if the vapor is either absent or composed of pure H_2O . The actual system, however, contains the base NaOH and the acid HCl in equivalent proportions since all the sodium and all the chlorine are introduced as NaCl , but the ratio of NH_3 to CO_2 is non-stoichiometric and variable. Despite the equality of total sodium and total chloride in the total system, the analysis of a solution from which NaHCO_3 has been precipitated requires four independent determinations, and hence the system is quinary, with or without a vapor phase.

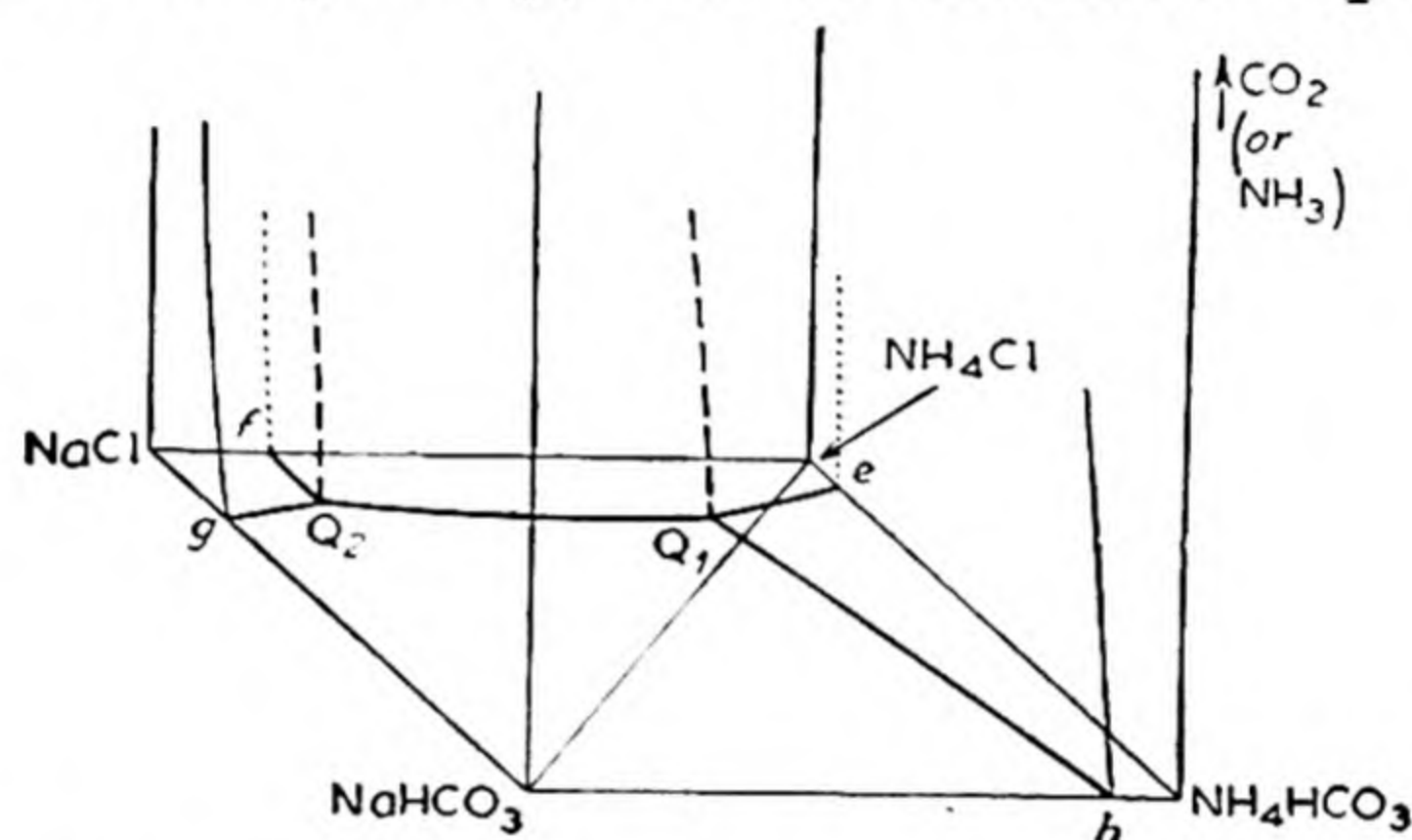


FIG. 18-13. Schematic isotherm for quinary system of type B.

The system may therefore be considered as the reciprocal salt pair $\text{NaCl} + \text{NH}_4\text{HCO}_3 \rightleftharpoons \text{NaHCO}_3 + \text{NH}_4\text{Cl}$, + water, + CO_2 or NH_3 , whichever is in excess. The compositions of the saturated solutions may then be represented by a square prism (Fig. 18-13), the base of which is the Jänecke diagram or polyhydric projection (Fig. 17-18) of the aqueous system of the reciprocal salt pair. Each side face of this isobaric isothermal diagram, which represents only the proportions of solutes in saturated solution, may be thought of as representing the effect of the concentration of CO_2 (or NH_3) in the solution, on the solubility equilibria in the four quaternary systems consisting of $\text{H}_2\text{O} + \text{CO}_2$ (or NH_3) + a pair of salts with common ion. If the solid phases remain the same four salts, a horizontal section of this diagram would have the same general appearance as the base, but would show the effect of excess of CO_2 (or NH_3), in solution, on the curves and points. The effect of pressure on the solid-liquid equilibria is essentially the same — that is, negligible — as in other aqueous salt systems at constant *composition*. The pressure, however, becomes a significant variable because the concentration of the CO_2 (or NH_3) in the liquid phase depends upon its pressure in the gas phase. This affects the water content of the solution, or the ratio of the four components here plotted, to

the water. But it is only the relative proportions of four substances (water ignored) that can be plotted in three dimensions. The vertical axis of the figure is, therefore, not to be confused with a pressure axis, although at any fixed temperature both the water content and the proportions of the solutes vary with the pressure of the gas phase, so that the solubility relations vary significantly with both P and T .

C. Type C: Aqueous Quinary Systems of Reciprocal Salts

1. Schematic Diagrams

Systems of water and six salts containing altogether five different radicals form the most important type of quinary system studied. Such systems, with two ions of one sign and three of another, are exemplified by the principal five-component system of the so-called "oceanic salts": $\text{H}_2\text{O} + \text{NaCl} + \text{KCl} + \text{MgCl}_2 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{MgSO}_4$.

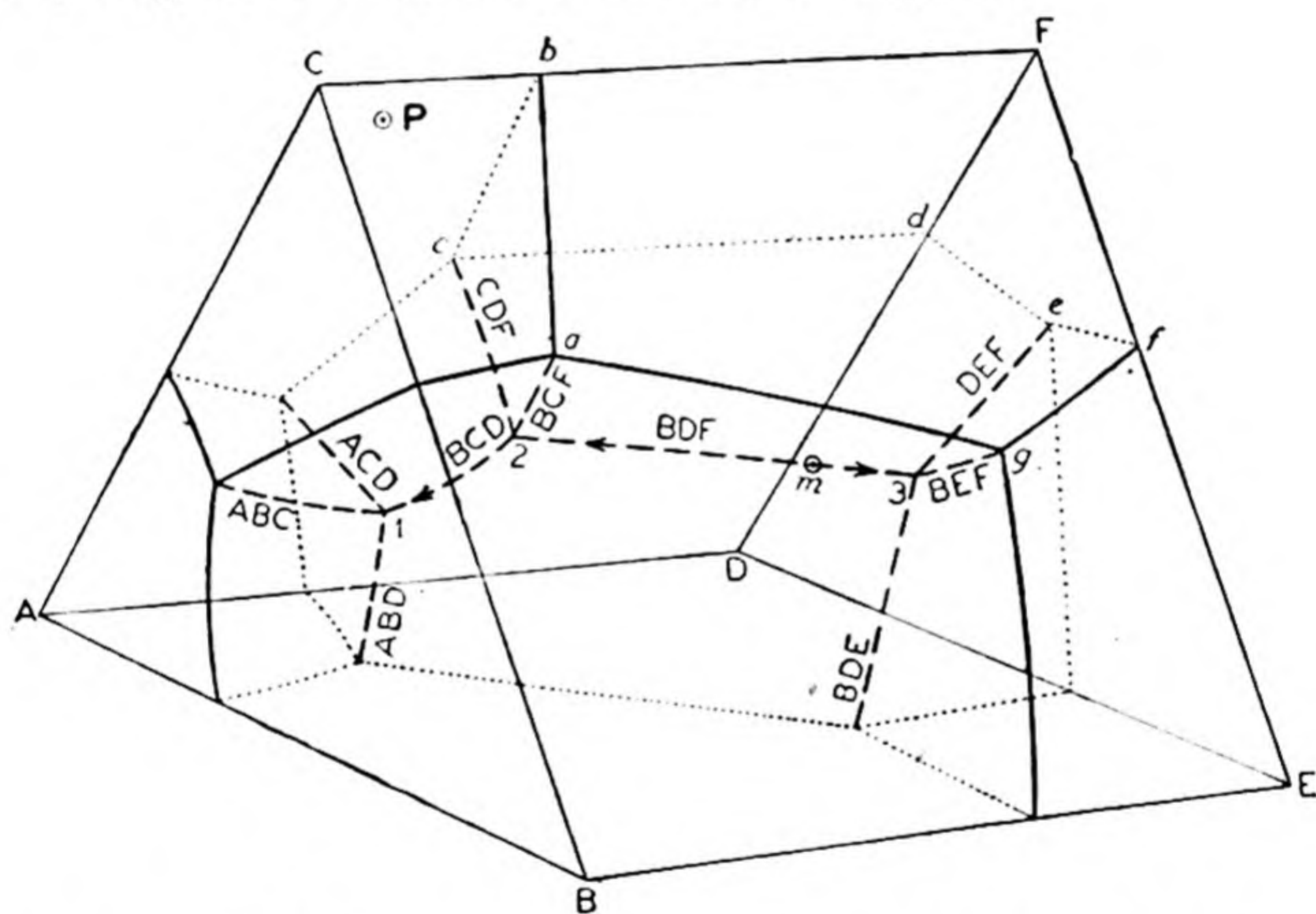


FIG. 18-14. Aqueous quinary system of reciprocal salts.

A system of this type involves three reciprocal salt pairs and two sets of three salts with common ion, and hence five quaternary aqueous systems. The isobaric isothermal model for the representation of the salt proportions of the saturated solutions is a triangular prism (Fig. 18-14). Here the salts A, B, and C represent salts with a common ion, such as LX, MX, and NX; D, E, and F represent the set LY, MY, and NY. The four square sides are the Jänecke diagrams of the four quaternary aqueous reciprocal systems, and the two equilateral triangular sides are the Jänecke diagrams of the additive systems of water + 3 salts with common ion. The units are equivalents, and the model is accompanied, in use, by a table giving the water content of all points plotted.

In the chemical analysis of such a quinary solution, it is necessary and sufficient to make four independent determinations: any three radicals and the water content, or any four radicals (that is, quantity per fixed weight of total sample). Again the two equations, Σ (weight percentages) = 100, and Σ (positive equivalents) = Σ (negative equivalents), then make possible the calculation of the complete composition. As in Chapter XVII, the data may be expressed in various final forms for plotting. The clearest procedure, in general, is the following. The proportions of the three radicals L, M, and N, among themselves, may be plotted on a triangular side of the prism, and the fraction of X in (X + Y) may then be plotted on the distance between the triangular sides, thus fixing an interior quinary point. The water content (weight percentage, or grams per 100 equivalents of total salts, etc.) is tabulated separately, for each point.

If no double salts are formed,² there are six spaces of saturation with single solid, twelve surfaces of twofold saturation, ten curves of threefold saturation, and three isothermally invariant points for liquid + 4 salts. The threefold saturation curves of Fig. 18-14 are labeled with the three solids involved on each; the invariant points involve the salts A, B, C, and D at point 1; B, C, D, and F at point 2; and B, D, E, and F at point 3. The figure shows only one of the possible arrangements, which will depend on the pair stability, or the stable diagonals, of the reciprocal systems involved. In the case assumed, the salt B may saturate a solution together with any other salt of the system; this is also true of the salt D, and in a special sense these salts may be called the stable pair of the system. If double salts are involved, more spaces, curves, and points are introduced, but the principles remain the same and can be better understood from the hypothetical simple case of Fig. 18-14.

The simple relations of Fig. 18-14 are illustrated by the 20° isotherm of the aqueous system of the chlorides and nitrates of potassium, ammonium, and sodium,³ and by the 20° isotherm of the aqueous system of the chlorides

² The anhydrous salts of this system constitute by themselves a reciprocal quaternary system of the type called "double ternary" by Jänecke (E. Jänecke, *Z. phys. Chem.*, **82**, 1, 1913; Part II of the article). The prism of Fig. 18-14 is then the composition diagram of such a system, and may be used to represent the polythermal projection of the $(T/c)_P$ relations of the system, as in Fig. 16-10 for the additive quaternary system. The schematic polythermal projections of the freezing point relations for the various cases in which the number of possible solid phases in the "double ternary" system varies from one to six, are discussed by Jänecke in the article cited. Because of the analogy between the variable T for an isobaric quaternary system, and the variable of "water content" for the condensed isothermal quinary salt system, Jänecke's figure for the case of six solids in the quaternary system is identical, schematically, with the present Fig. 18-14.

³ H. Schütze, T. Piechowicz and B. Wahl, *Helv. Chim. Acta*, **26**, 233 (1943).

and bicarbonates of the same cations.⁴ In the first case the "stable pair," corresponding to $B + D$ of Fig. 18-14, is $\text{KNO}_3 + \text{NH}_4\text{Cl}$; in the second case it is $\text{KCl} + \text{NaHCO}_3$.

As usual, at least one of the three invariant points of Fig. 18-14 must be congruently saturated with its four salts, and hence must be a congruent drying-up point in isothermal evaporation; and the process of isothermal evaporation may be followed, from any point within the prism, in the manner already explained for the simpler, additive case of Fig. 18-1. In Fig. 18-15 the prism of Fig. 18-14 is divided into the three tetrahedra of four salts which may be obtained on complete isothermal evaporation of any quinary solution. The invariant points 1 and 2 are assumed to be in tetra-

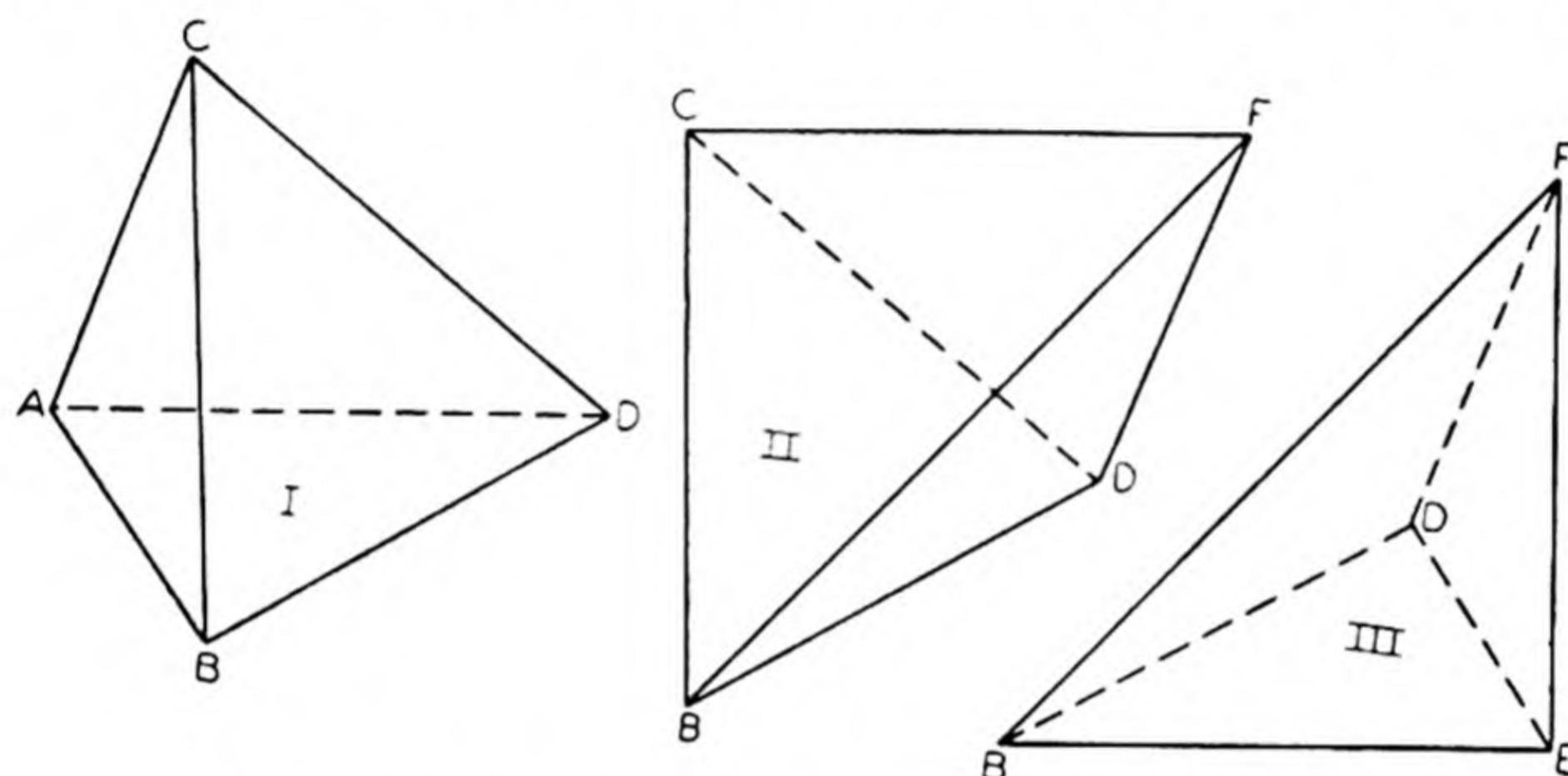


FIG. 18-15. Sub-tetrahedra of Fig. 18-14.

hedron I, and point 3 in III. Hence all solutions in III proceed to point 3, their congruent drying-up point; those in II must reach point 2 in I, as an incongruent drying-up point; and those in I dry up at point 1, although some of them (in the tetrahedron 2CDB) stop first at point 2, where salt F is consumed, before they proceed on curve 21.

Consider an unsaturated solution with salt proportions represented by point P (Fig. 18-14), falling in the space for saturation with C alone, but in tetrahedron I. As C separates during evaporation, the liquid composition changes along the line CP, away from C, and reaches, it will be assumed, the surface $abc2$, for saturation with $C + F$. As C and F precipitate together, the solution proceeds, on this surface, on a course fixed by the plane CFP, to one of the two curves, CDF or BCF, leading to the incongruently saturated point 2; we shall assume that it reaches curve BCF. It then proceeds on this curve, precipitating B, C, and F, to point 2, where the solid F is consumed, while D precipitates. The residual liquid, precipitating B, C, and D, now moves on the curve 21 to point 1, where it dries up invariantly to leave a mixture of A, B, C, and D in the proportions P.

⁴ H. Schütze, T. Piechowicz and W. Pustelnik, *ibid.*, 26, 237 (1943).

Both point 1 and point 3, being congruent drying-up points, are points of minimum "water content." On some point m , on the curve 23, the "water content" is a maximum for the curve, so that the direction followed by the liquids of threefold saturation on these interior curves, as shown in Fig. 18-14, will be away from m on both sides, toward point 3, a minimum, and toward point 2, whence the liquid may continue, with falling W_i , to point 1. Point m , a 4-dimensional isothermal, condensed "saddle point," lies at the intersection of the curve 23 with the plane BDF, which separates the tetrahedra II and III. It is a solution congruently saturated with the three salts B, D, and F.

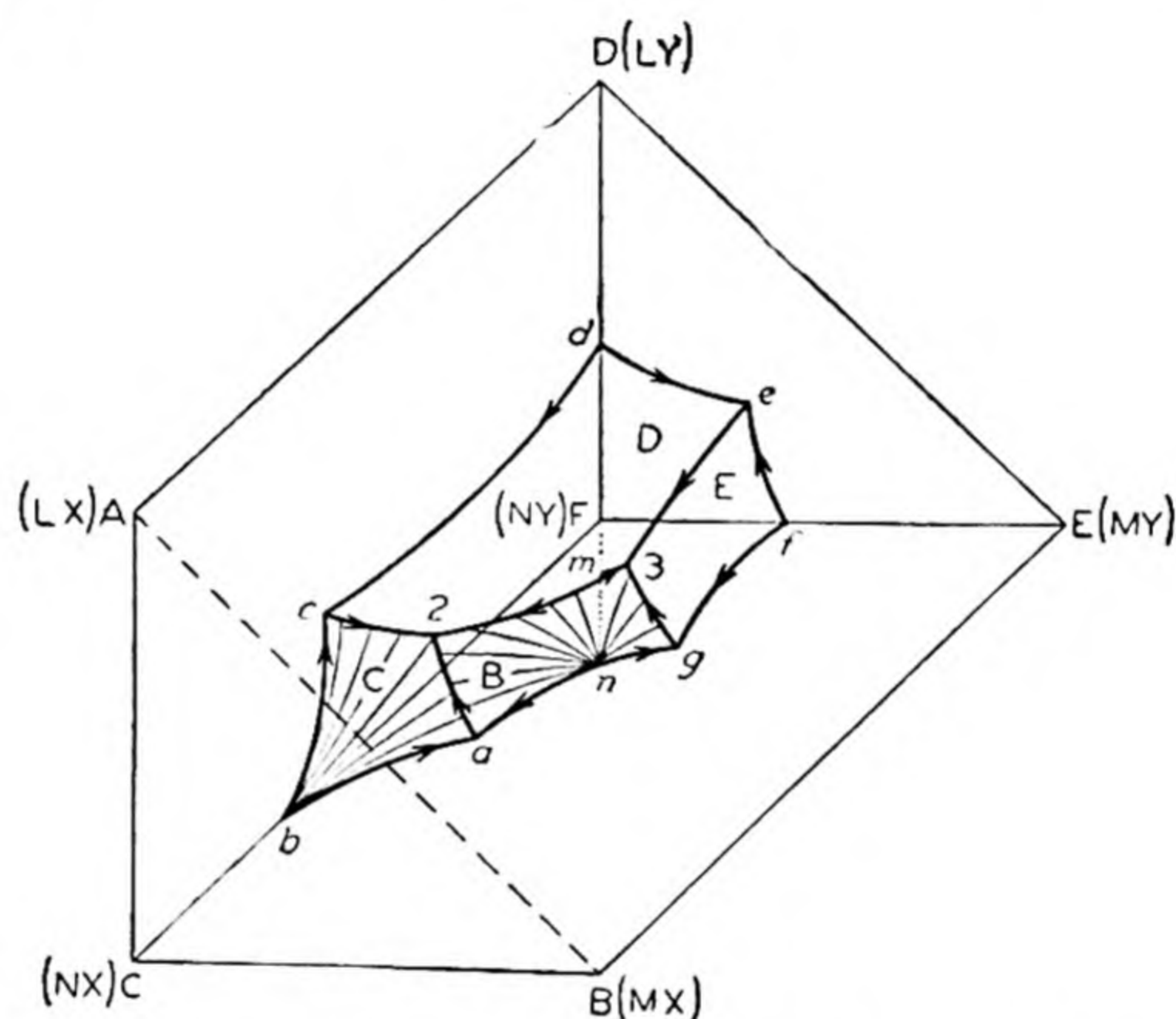


FIG. 18-16. Orthogonal projection of (inclined) prism of Fig. 18-14, showing solutions saturated with $F(NY)$ in common.

The compositions of solutions, saturated with a common salt in addition to one or more other salts, may again be shown by a projection on a plane, as in the construction shown in Fig. 18-16, for solutions saturated with salt F in common. For this purpose, the point F is imagined placed over the center of the square $ABED$ of Fig. 18-14, by suitably inclining the triangular faces of the prism. Looking down, then, upon the prism from the line CF (which lies horizontally above the plane of the paper), we see the edges of the prism as in Fig. 18-16, and the orthogonal projection of the surfaces bounded by $abcdefg$, for saturation with F as common phase. The projections of the crystallization paths on each surface of twofold saturation are curves, radiating for each field from a point on the exterior solubility curve where the salt proportions (disregarding F , or NY) are those of the separating second solid, and hence from points b , d , and f for the fields C , D , and E , respectively. In the B field, the paths radiate from the point n

on the line DFB, which therefore includes the point m ; n is a quaternary solution, in the system MX–NY–H₂O, congruently saturated with the stable pair MX + NY, corresponding to m in Fig. 17–7.

In order to plot a quinary composition on this projection, the square ABED is treated somewhat as in Fig. 15–5(a), the half-diagonal, or line FD, being taken as 100% of dissolved salts. Then the salt proportions are expressed as equivalent percentages of the four salts F, C, D, and E, or NY, NX, LY, and MY. This means that the quantity of X found in the chemical analysis is all calculated as NX, L as LY and M as MY, so that while the equivalent percentages of the salts C, D, and E are always positive, that of F, or NY, may be either positive or negative. In plotting the projection the percentage of D is measured upward on FD, and %E is then measured to the right, with the same scale, parallel to FE. The percentage of C is then measured, from the resulting point, toward C parallel to FC, but after it has been multiplied by $\sqrt{2}$, since $FC = \sqrt{2}(FD)$. Reading back from the plot to the proportions of the plotted salts is, as usual, not a direct procedure and requires knowledge of the percentage of F. If the equivalent percentage of F is known, a plotted point **P**, such as the invariant point 3, is extended to **P'** as usual, by the method of parallels, so that $100 \text{ PP}'/\text{FP}' = \%F$. Then the relative proportions of C, D, and E among themselves may be read from the position of **P'** in the composition triangle (isosceles but not equilateral) CDE. The line CP' extended to the base DE of this triangle gives there the ratio of D to E; and the perpendicular distance of **P'** from DE relative to the corresponding distance of point C from DE gives the ratio of C to C + D + E. If %F is negative, the “extended” point **P'** lies between **P** and the origin F, still however at such a distance that $100 \text{ PP}'/\text{FP}' = |\%F|$. [If all quinary compositions in Fig. 18–14 are expressed in terms of C, D, E, and F, then the percentage of F is positive above the plane CDE or in the tetrahedron CDEF, and negative below that plane or in the space ABCDE. When the diagram is projected radially from the corner F all compositions, however, appear in the triangle CDE. Therefore, while the orthogonal projection of the inclined prism covers the area CADEB of Fig. 18–16, the perspective projection from point F, with either positive or negative percentage of F, must appear, in the same figure, in the triangle CDE. When the orthogonal point **P** is “extended,” then, in the manner indicated, to the perspective point **P'**, **P'** gives the relative proportions of C, D, and E among themselves in the composition triangle CDE.]

The data are also often plotted by methods not related to the finite model of Fig. 18–14. In the manner of a Löwenherz diagram, for example, the three axes of Fig. 18–16 may be used to plot the concentrations in units of

number of equivalents of each of the three salts C, D, and E (F being ignored in the plot) per 1000 moles of water. The resulting diagram will resemble the orthogonal projection of Fig. 18-16, but will not be the same. In the method of D'Ans, the three axes of Fig. 18-16 are made to intersect at 120° , their scales are made equal, and the data are plotted directly in equivalents of each of the three salts indicated, per 1000 moles of water. The appearance of this diagram is also similar to that of Fig. 18-16, and the crystallization paths are still curved.

If, finally, we ignore the concentration of salt F, the common saturating solid, the proportions of the other three salts, C, D, and E, among themselves may be plotted as usual in a Jänecke type of diagram, such as Fig. 18-17. For the plotting of Fig. 18-17, the analytical data must similarly

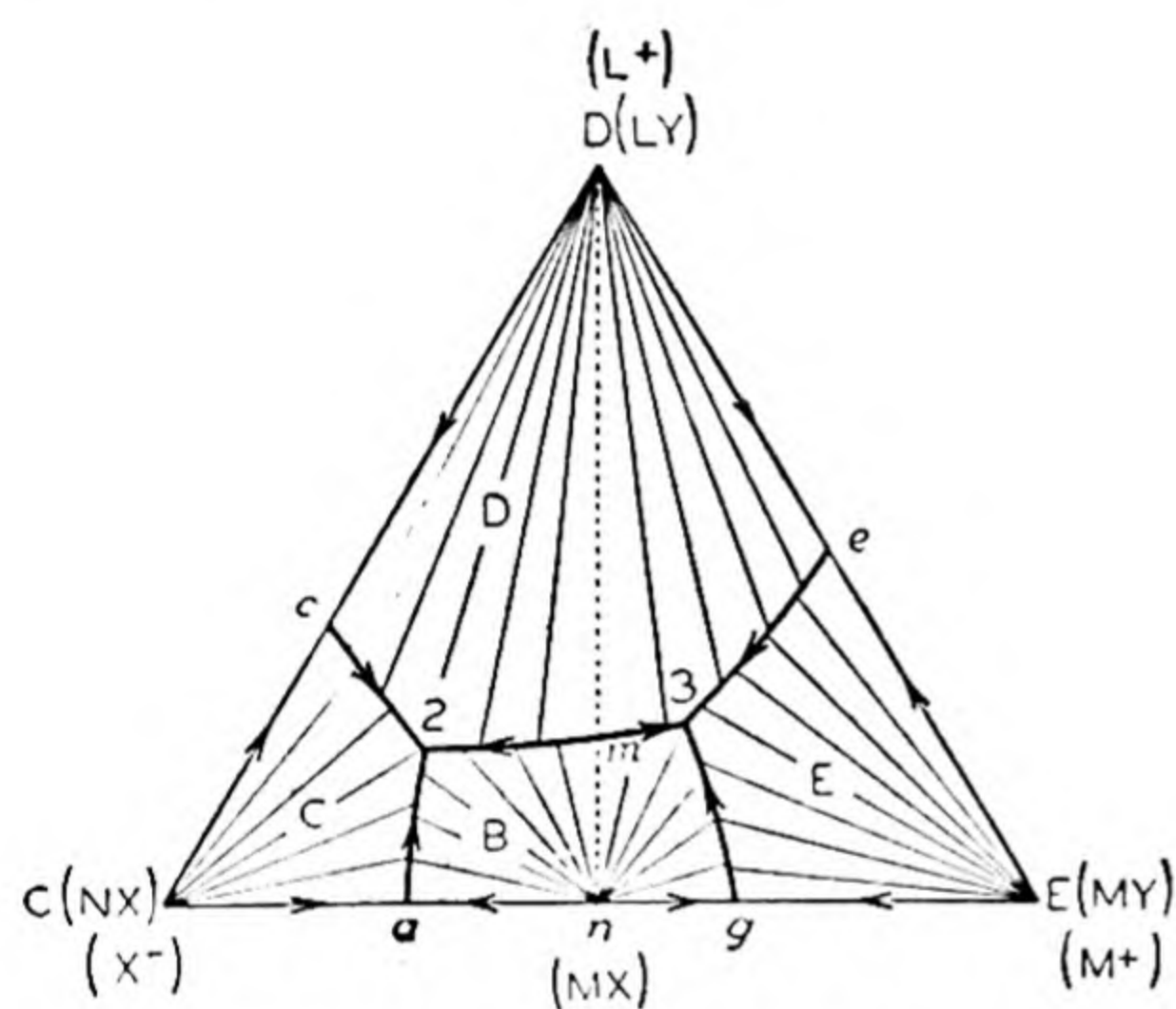


FIG. 18-17. Jänecke diagram for solutions saturated with F(NY) in common.

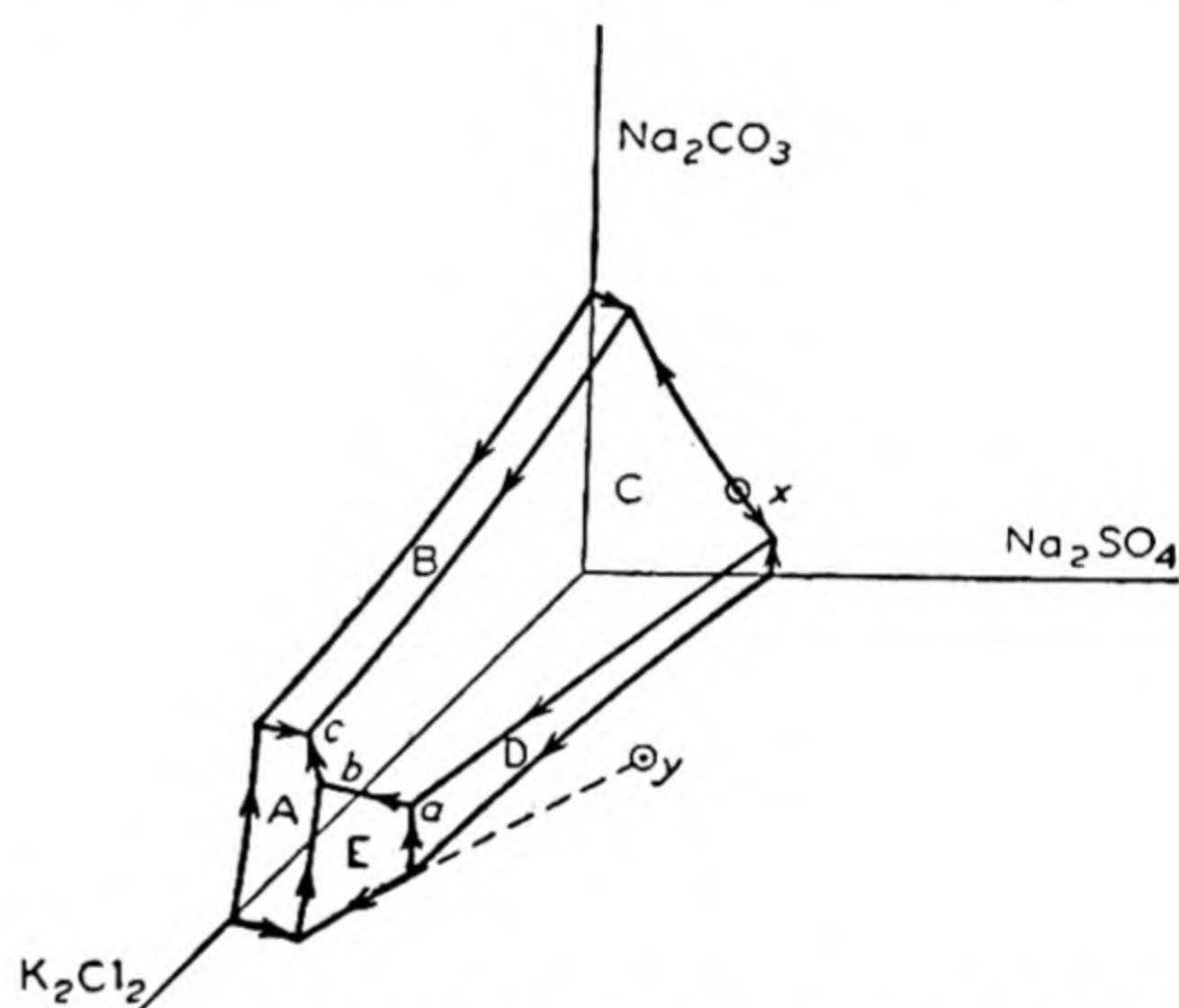


FIG. 18-18. System water + chlorides, sulfates and carbonates of sodium and potassium, at 75° ; saturation with NaCl; Löwenherz type of diagram (schematic).

be expressed in terms of the salts NX (C), LY (D), MY (E), and NY (F, the common saturating salt). All the radical X is calculated as NX, all the L as LY, and all the M as MY, so that these salts will necessarily be represented as positive quantities, while the quantity of the common, saturating salt may or may not be positive. Thereupon, with both water content and proportion of the salt NY neglected, the relative proportions of the three salts indicated, in solutions saturated in common with NY, are shown in Fig. 18-17. Now the crystallization paths are straight lines. In the B field they radiate from the mid-point of the base since the precipitation of MX (=B) removes the radicals X and M in equivalent proportions. This diagram clearly fixes in general the position of a congruently saturated solution such as *m* on the curve 23, and hence the direction followed by liquids

on that curve. (The particular point m here involved is, of course, also fixed by Fig. 18-16, but only because it falls on one of the diagonals of that figure.)

This convenient diagram may be said to plot the proportions of the three ions X^- , L^+ and M^+ in the solutions saturated with NY as common solid phase, and the corners NX , LY , and MY may be labeled X^- , L^+ , and M^+ , respectively. But it must be remembered that what is separating along a crystallization path in the E field, for example, is the substance E ($=MY$), and it is better to label the corners as substances, in accordance with the way in which the analytical data can be expressed, as explained above.

2. Example; Double Salts

Fig. 18-18 shows the system water + the chlorides, sulfates and carbonates of sodium and potassium,⁵ plotted on the coordinate axes of Fig. 18-16, but as in a Löwenherz diagram, in units of equivalents per 1000 moles

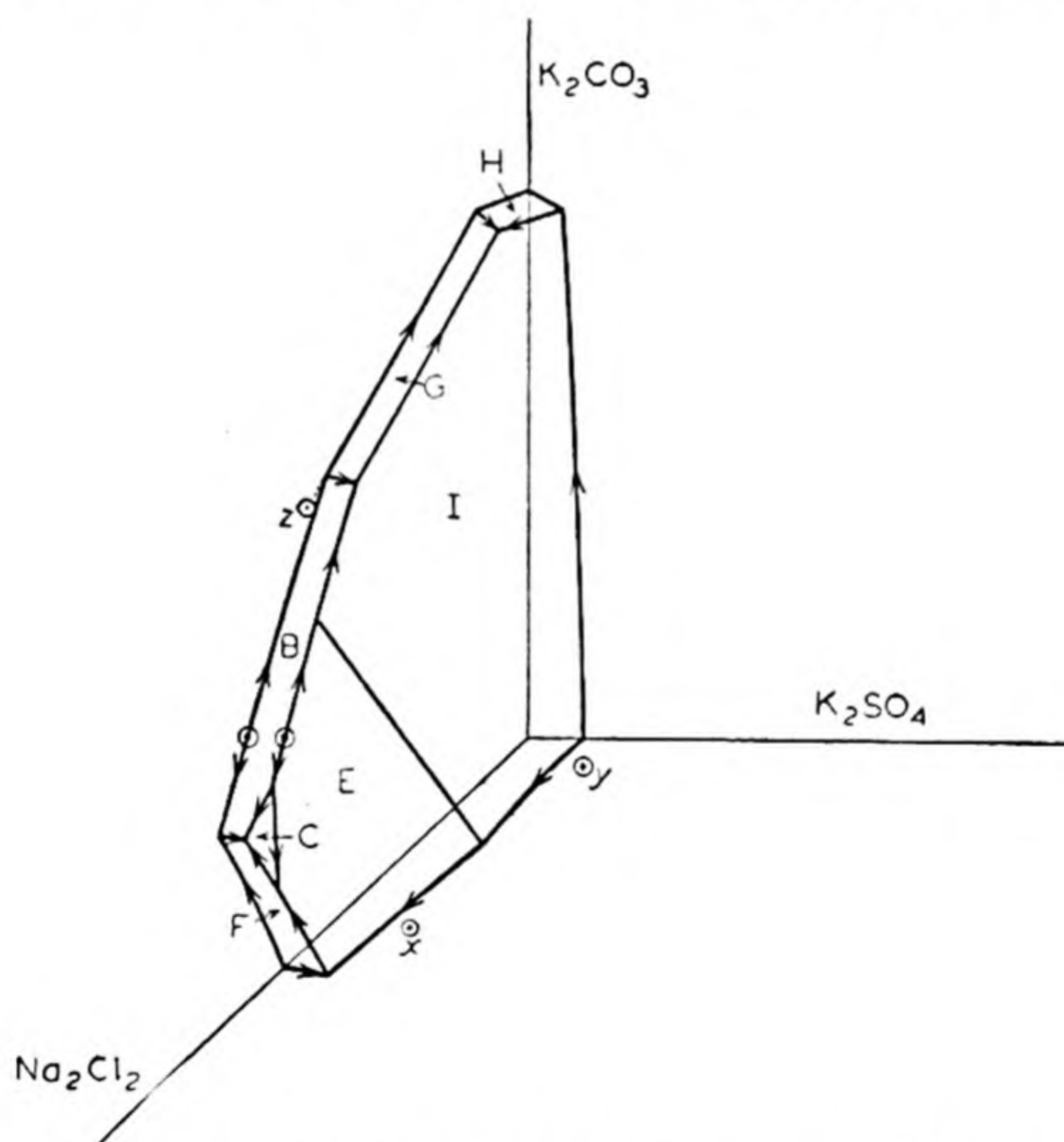


FIG. 18-19. Same isotherm as Fig. 18-18, but for saturation with KCl in common (schematic).

of water, showing the compositions of solutions saturated, at 75° , with $NaCl$ together with the following salts: A, KCl ; B, $Na_2CO_3 \cdot H_2O$; C, burkeite, $Na_2CO_3 \cdot 2Na_2SO_4$; D, Na_2SO_4 ; E, glaserite, $Na_2SO_4 \cdot 3K_2SO_4$. The points x and y , for the origins of the crystallization paths in the C and E fields, respectively, are located by extrapolation as explained under Fig. 18-9. Fig. 18-19, plotted in the same manner, shows the solutions

⁵ Teeple, *loc. cit.*, pp. 100-111. The dimensions have been distorted, for purposes of clarity, in Figs. 18-18 and 18-19, which are therefore schematic.

saturated with KCl as common phase, at the same temperature; the additional solids appearing in Fig. 18-19 are: F, NaCl; G, $\text{Na}_2\text{CO}_3 \cdot \text{K}_2\text{CO}_3$ (point z); H, $\text{K}_2\text{CO}_3 \cdot 3/2\text{H}_2\text{O}$; I, K_2SO_4 . In Fig. 18-20, the projection of Fig. 18-18 is transformed to a Jänecke diagram, according to the method of Fig. 18-17. Now the points x and y fixing the direction of the crystallization paths in the C and E fields are found without extrapolation. The diagram may be considered to represent the proportions of the ions $(\text{K}^+)_2$, $\text{CO}_3^{=}$ and $\text{SO}_4^{=}$. Hence point x (burkeite) is located one-third of the way from the Na_2SO_4 corner to Na_2CO_3 , and point y (glaserite) at three-sevenths of the way from Na_2SO_4 to K_2Cl_2 .

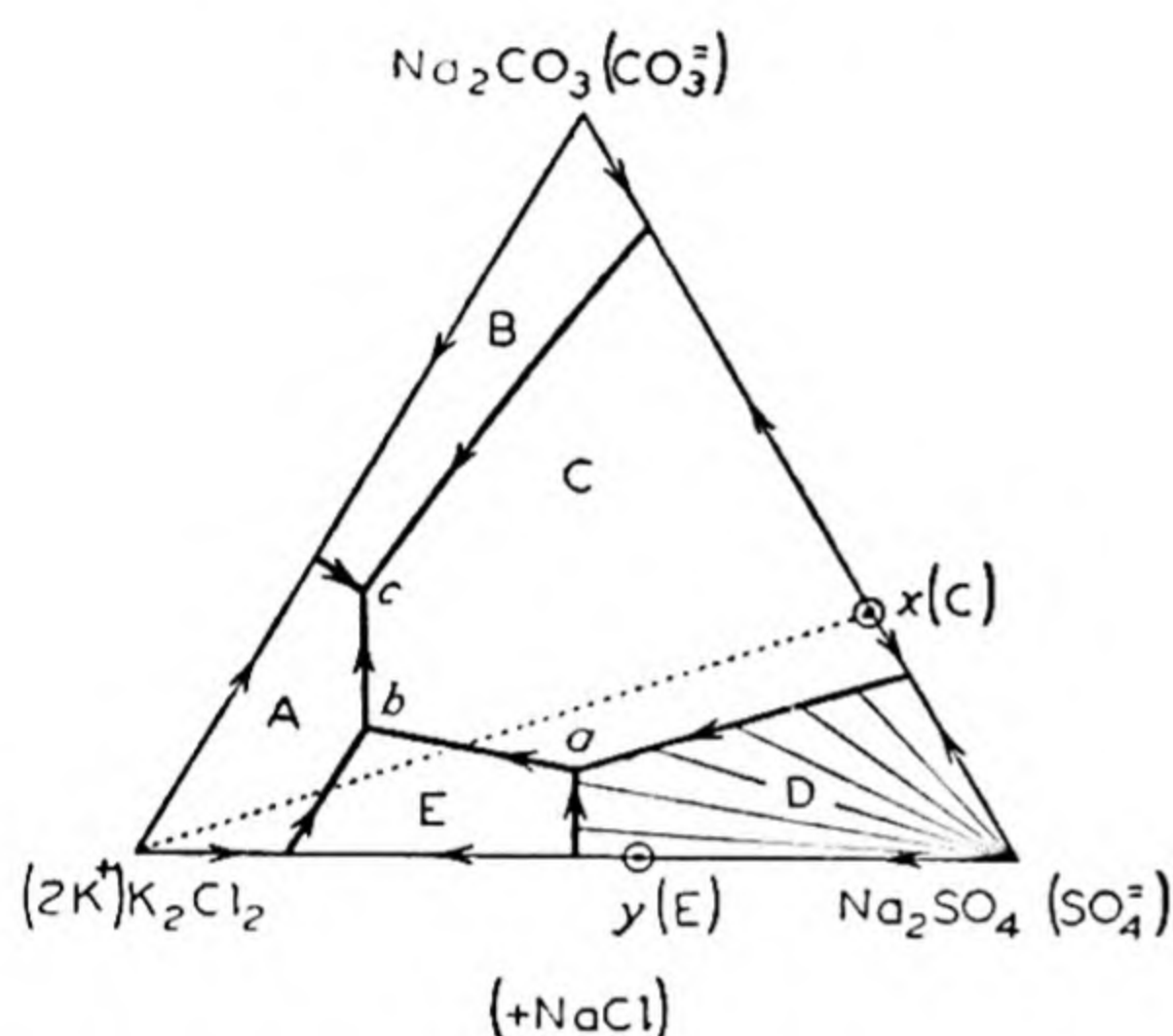


FIG. 18-20. Jänecke diagram for Fig. 18-18.

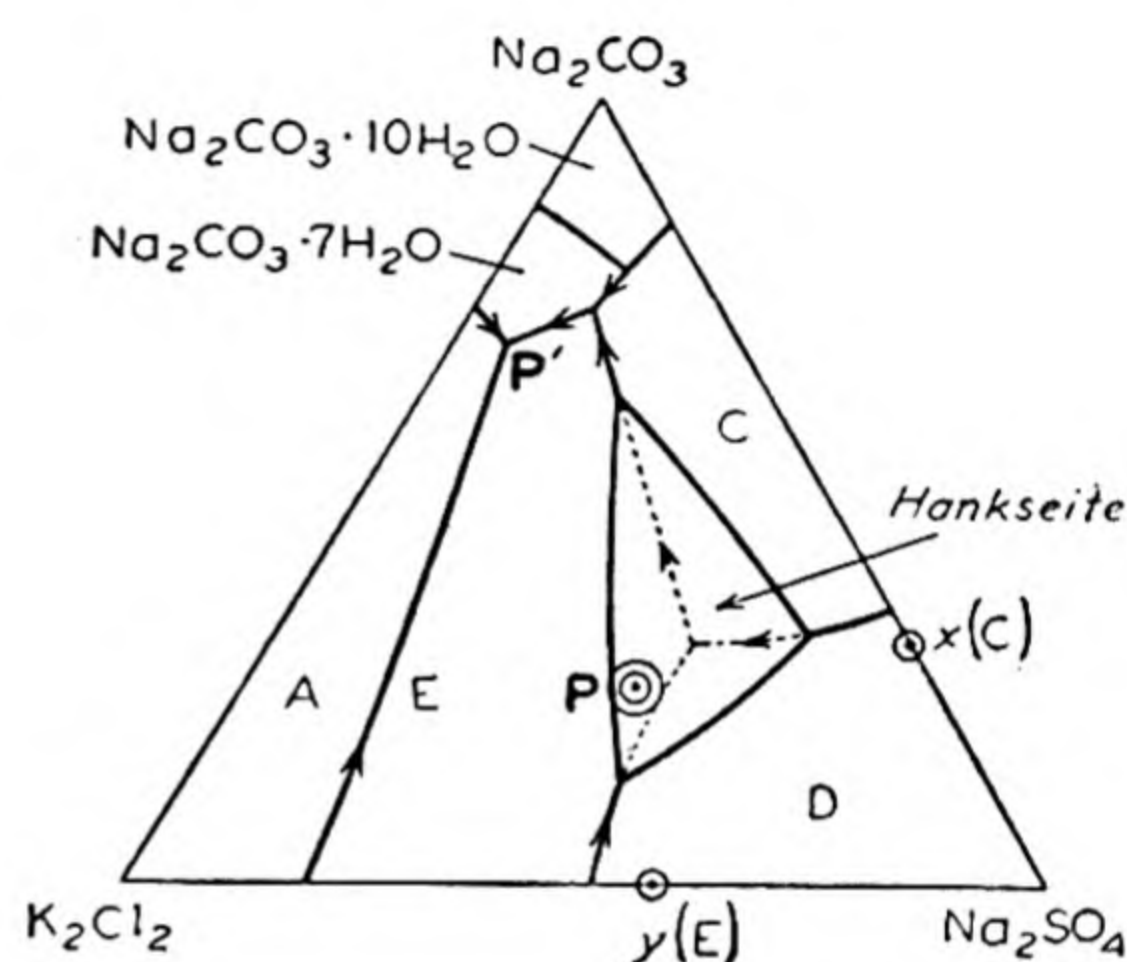


FIG. 18-21. Same system, at 20°; saturation with NaCl in common.

The 100° isotherm for the same system, for saturation with NaCl as the common phase, is very similar to Fig. 18-20 at 75°. The 20° isotherm for NaCl saturation, on the other hand, is that shown in Fig. 18-21. The tetragene salt, hankseite, $\text{KCl} \cdot 2\text{Na}_2\text{CO}_3 \cdot 9\text{H}_2\text{O}$, forms only with difficulty, and the usual relations are the metastable equilibria indicated by the dotted curves. The brine of Searles Lake, saturated with NaCl, is represented by point P, in respect to the proportions of the three ions $(\text{K}^+)_2$, $\text{CO}_3^{=}$, $\text{SO}_4^{=}$. It is clear that evaporation at 20° would precipitate glaserite (E) so that most of the potassium would be obtained in the unwanted form of K_2SO_4 (in glaserite) before the KCl field (A) could be reached. If the evaporation is carried out at 100°, however, the point P lies in the burkeite field (C, or $\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$), and with the separation of this salt the liquid moves across to a point, z , near b on the curve bc of Fig. 18-20, before KCl would precipitate, mixed with burkeite. If the burkeite is now removed and the liquid is cooled to 20°, its composition lies in the KCl field at this lower temperature, whereupon KCl can be obtained (always accompanied

with some NaCl), until the solution reaches some boundary of the KCl field near point P' of Fig. 18-21, the final drying-up point at 20° for saturation with NaCl.⁶ These relations are shown in Fig. 18-22 (schematic), which superimposes the 100° and the 20° isotherms. This diagram is to be compared with Fig. 17-20, the difference being

that the present one represents saturation with an additional phase at every point.

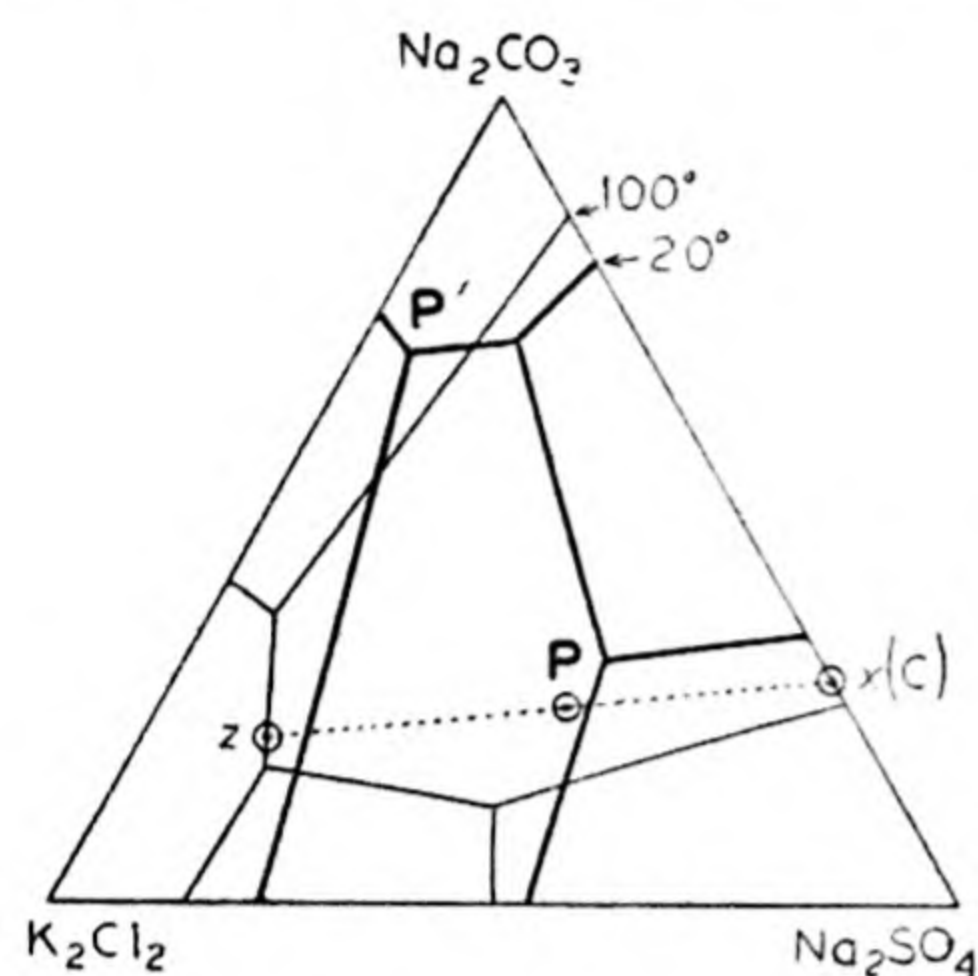


FIG. 18-22. Separation of KCl (mixed with some NaCl) from Searles Lake brine; schematic diagram.

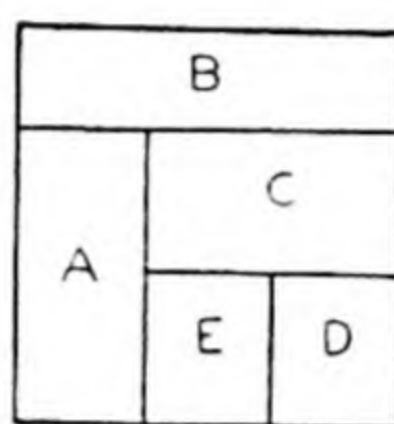


FIG. 18-23. Paragenetic diagram of Fig. 18-18.

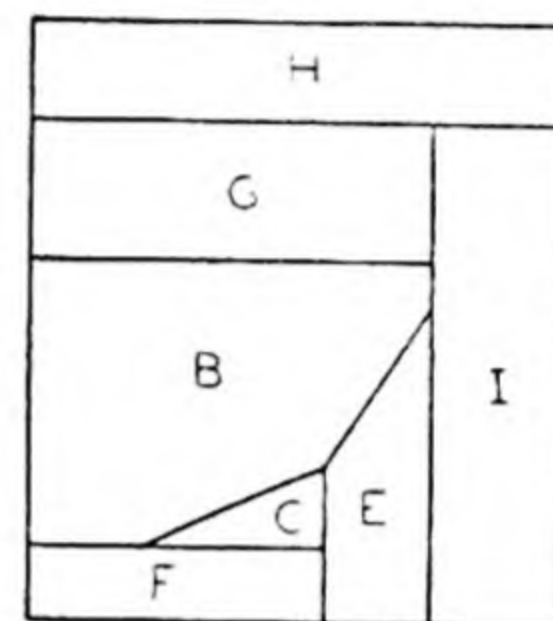


FIG. 18-24. Paragenetic diagram of Fig. 18-19.

Finally, if a number of isotherms, plotted as Jänecke diagrams, are laid one upon the other, spaced according to temperature, a T/c prism of the quinary system may be constructed, in which the corresponding isothermally invariant points are joined into curves of fourfold saturation, with respect to the three salts actually plotted, plus a specified, common saturating salt, such as NaCl, not plotted. A space in this prism represents saturation with two salts, while a point, or intersection of four curves of fourfold saturation, is a condensed invariant point for solution + 5 salts (+ vapor).

Qualitative representations of the relations shown in figures such as Figs. 18-18 and 18-19, sketched in the fashion of Figs. 18-23 and 18-24, are known as **paragenetic diagrams**, as used by van't Hoff.⁷ They are used to follow the schematic changes in the equilibria of the system, always while saturated with the specified common phase, as the temperature may be changed (paragenesis or transformation of salts) by simple comparison of such diagrams.

D. Note on Systems of Six Components

An aqueous system composed of various salts, acids, and bases, which because of the phase reactions involved in the phenomena under study requires five independent analytical determinations for the establishment of the composition of the solution, is a six-component system. As pointed out

⁶ G. R. Robertson, *Ind. Eng. Chem.*, **21**, 520 (1929).

⁷ J. H. van't Hoff (Ref. U).

above under the ammonia-soda system, stoichiometric restrictions between individual acids and bases in the total system may turn out not to be restrictions in the actual analytical problem, because of "double decompositions." Hence the following general cases may be enumerated as possibilities. (1) An aqueous system made up from salts with six different ions, so that there is total restriction between the base and acid equivalents, and involving no hydrolysis: (a) additive, with five salts having a common ion; (b) reciprocal, with two ions of one sign and four of another; (c) reciprocal, with three ions of each sign. (2) Aqueous system of one base (or acid) and four acids (or bases) with no total restriction, despite even as many as three individual restrictions, as when the system is made up from water, three salts with common cation, and a foreign acid. (3) Aqueous system of two bases (or acids) and three acids (or bases) without total restriction.

The studies on six-component systems are all incomplete. The number of lower order systems, ternary, quaternary and quinary, comprising a six-component system, particularly a reciprocal one, is very large. If the variables of P , T , and water content are neglected, the salt proportions of saturated solutions would require a 4-dimensional figure for their representation. A 3-dimensional figure, usually quite complicated, is required for the "projection" of the salt proportions in solutions saturated with a common salt in addition to one or more other salts. A plane projection of this figure may then be constructed for the salt proportions — now neglecting three composition variables, two salts, and water — for solutions saturated with two salts in common in addition to one or more others. In principle and in general appearance, the resulting diagram is similar to Figs. 18-18, and 18-19.

The most thoroughly studied system has been that of the chlorides and sulfates of sodium, potassium, magnesium, and calcium, the principal constituents of sea water and of the Stassfurt salt deposits.^{7, 8} The complexity of the isothermal relations at 25° may be appreciated by noting that the number of fields for solutions saturated with NaCl and one other solid, in one of the six auxiliary quinary systems (namely Na^+ , K^+ , Mg^{++} , Cl^- , $\text{SO}_4^{=}$, H_2O), is twelve. Nevertheless some of the important features of the isothermal relations of the six-component system, such as the conditions for saturation with NaCl and some calcium salt (such as gypsum, anhydrite, syngenite, polyhalite, and pentasalt) as two common saturating salts, have been elaborated at 0°, 25°, 55°, and 83°, and used in the interpretation of the geological record of the salt deposits.⁹

⁸ J. D'Ans (Ref. A).

⁹ For some discussion, see Blasdale, Ref. C, Chapters 9 and 10.

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(The symbol W in this index represents water, not tungsten.)

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